U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-284 859

Investigation of Matrix Interferences for AAS Trace Metal Analyses of Sediments

Gulf South Research Inst, New Orleans, La

Prepared for

Environmental Monitoring and Support Lab -Cincinnati, Ohio

May 78

United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Cincinnati OH 45268

EPA-600/7-78-085
May 1978

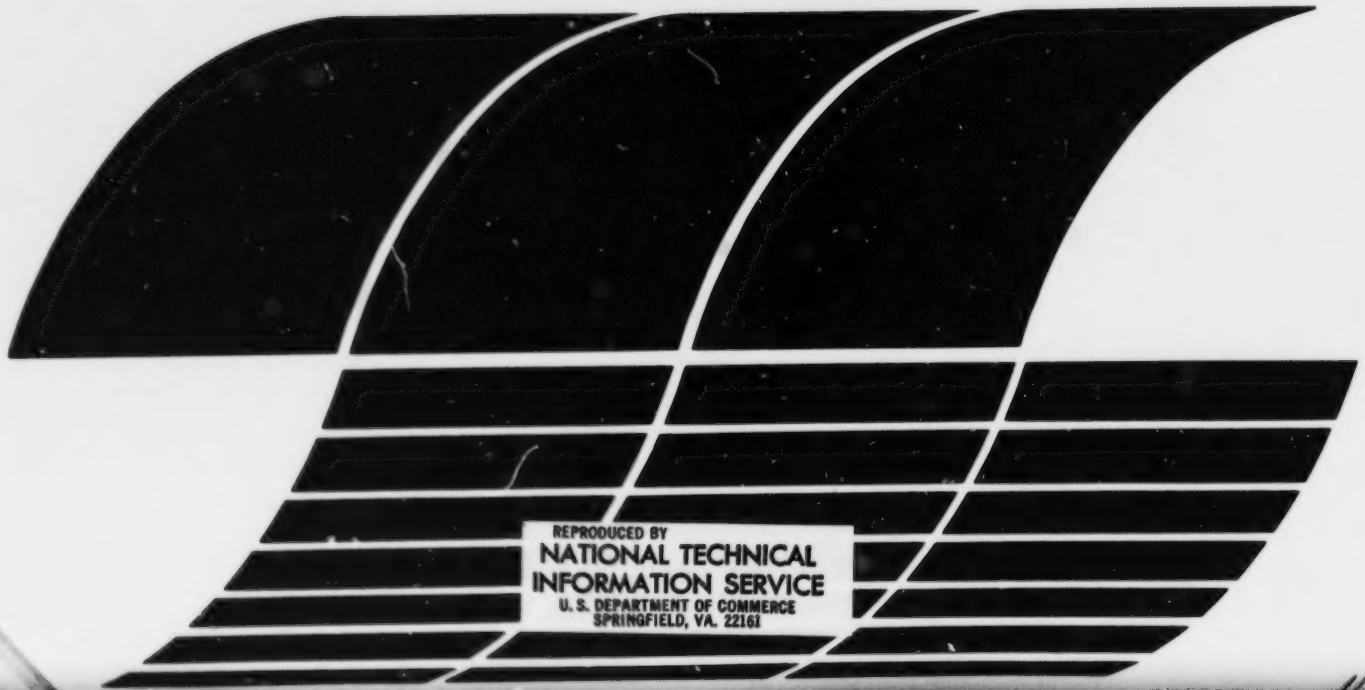
Research and Development

PB 284 859

EPA

Investigation of Matrix Interferences for AAS Trace Metal Analyses of Sediments

Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-78-085	2.
3. RECIPIENT'S ACCESSION NO. PB284859	
4. TITLE AND SUBTITLE Investigation of Matrix Interferences for AAS Trace Metal Analyses of Sediments	5. REPORT DATE May 1978 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Mary M. McKown, Charles R. Tschirn and Patty P.F. Lee	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Gulf South Research Institute P.O. Box 26518 New Orleans, LA 7-186	10. PROGRAM ELEMENT NO. EHE 625
	11. CONTRACT/GRANT NO. R 804317-01
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Lab. -Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/06
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

This research program was initiated with the overall objective of developing reliable, cost-effective methods utilizing flame atomic absorption spectrophotometry for the trace elemental analysis of soil and sediment samples containing complex matrices. The soil sample matrix studied consisted of more than 0.1 percent aluminum and iron; the sediment sample matrix contained more than 0.1 percent aluminum and iron plus lesser quantities of calcium, magnesium, manganese, phosphate and potassium.

Conventional flame AAS methods were found to produce accurate results for the analyses of cobalt, copper, lead, manganese, nickel and zinc in these matrices. The barium, calcium, strontium and vanadium content of these samples could not be accurately determined by conventional flame AAS techniques. However, reliable results were obtained using appropriate flame types with the addition of lanthanum and/or an easily ionizable alkali salt to all samples and standards.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Cobalt, copper, lead, manganese, nickel, zinc, barium, calcium, strontium, vanadium .	Sediment Analysis Trace Metals Atomic Absorption	99A 99E

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 149
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE PC A07/MF A01

EPA Form 2220-1 (9-73)

★ U.S. GOVERNMENT PRINTING OFFICE: 1978— 757-140/6852

PROCEDURE FOR METAL ANALYSIS OF SEDIMENTS

Environmental Protection Agency
Region IV, Surveillance and Analysis Division
Chemical Services Branch

Tentative Digestion of Sediments for Metal Analysis
June 28, 1973

1. Weigh 1 to 2 g of dry (103°C) sediment into a 250 ml Erlenmeyer flask.
2. Add 50 ml water, 0.5 ml conc HNO_3, and 5 ml conc HCl.
3. Heat at 95°C for 15 min.
4. Cool and clarify sample by filtering or centrifuging.
5. Dilute to 100 ml.
6. Proceed with atomic absorption analyses for Pb, Zn, Mn, Cd, Cu, Ni, and Cr.

GSRI ALTERATIONS*

1. 4 g of dry sediment was used.
2. 75 ml of water, 1.0 ml conc. HNO_3, and 10 ml conc. HCl were added.
3. Heating at 95°C was continued until volume was reduced to 10 to 15 ml (approximately 3 hr).
4. Filtration rather than centrifugation was performed.
5. The final dilution volume was 50 ml.

*Changes described were effected in order to improve accuracy and detection limits.

EPA-600/7-78-085
May 1978

INVESTIGATION OF MATRIX INTERFERENCES FOR AAS TRACE METAL ANALYSES OF SEDIMENTS

by

Mary M. McKown
Charles R. Tschrin
Patty P.F. Lee

Gulf South Research Institute
New Orleans, Louisiana 70186

EPA Grant No. R 804317-01

Project Officer
John F. Kopp
Physics and Chemistry Methods Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water. Conduct studies to determine the responses of aquatic organisms to water quality.
- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

The standard methods for analysis of water and waste samples are under continual review to assure that the most accurate results possible are obtained. If a chemical interference in an important analytical procedure is discovered it must be evaluated and, if necessary, a procedural modification made to circumvent the interference. This report investigates the interference of sediment matrices on trace metal analyses by atomic absorption spectrophotometry.

Dwight G. Ballinger
Director
Environmental Monitoring and Support
Laboratory

ABSTRACT

This research program was initiated with the overall objective of developing reliable, cost-effective methods utilizing flame atomic absorption spectrophotometry (AAS) for the trace elemental analysis of soil and sediment samples containing complex matrices. The soil sample matrix studied consisted of more than 0.1 percent aluminum and iron; the sediment sample matrix contained more than 0.1 percent aluminum and iron plus lesser quantities of calcium, magnesium, manganese, phosphate, and potassium.

Conventional flame AAS methods were found to produce accurate results for the analyses of cobalt, copper, lead, manganese, nickel, and zinc in these matrices. The barium, calcium, strontium, and vanadium content of these samples could not be accurately determined by conventional flame AAS techniques. However, reliable results were obtained using appropriate flame types with the addition of lanthanum and/or an easily ionizable alkali salt to all samples and standards. Interferences present in the analyses of beryllium, chromium, and titanium were difficult to correct in samples containing large concentrations of interfering matrix constituents. The use of matrix-matched standards was recommended for samples of this type. The analysis of selenium was performed using a nitrous oxide-acetylene flame. However, the detection limit obtained with this technique may not be sufficient for many applications because small concentrations of selenium are very toxic. Direct AAS analysis of selenium using lower-temperature flame types was affected by interferences that were not corrected by those techniques chosen for investigation. Correction of these interferences was therefore beyond the scope of this research effort.

Procedures used in this research should be applicable to all environmental samples containing similar matrices. Information provided in this report will permit adaptation of these techniques to samples other than those examined here.

This report is submitted in fulfillment of Grant No. R 804317-01 by Gulf South Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 1, 1976, to November 30, 1977; work was completed on September 30, 1977.

CONTENTS

Foreword..... iii
Abstract..... iv

1. Introduction..... 1
2. Conclusions and Recommendations..... 2
3. Sample Collection..... 4
    Site selection..... 4
    Collection of samples..... 6
4. Experimental Procedures..... 7
    Glassware cleaning..... 7
    Reagents and standards..... 7
    Apparatus..... 7
    Sample preparation..... 7
    Quality control..... 8
5. Results and Discussion..... 9
    Initial analyses..... 9
    Interference study..... 10
    Final analyses..... 21
    Quality control procedures..... 21
6. Figures and Tables..... 24

References..... 129

SECTION 1

INTRODUCTION

The emphasis of this research was to develop accurate, cost-effective flame atomic absorption spectrophotometric (AAS) methods for the analysis of trace metals in complex matrices. Bottom sediment subjected to acid mine drainage and soil receiving fallout from a coal-fired power plant were employed for this investigation.

Because the production and usage of energy from coal, gas, and oil are major sources of trace metal pollution, the current energy crisis has meant increased emphasis on environmental monitoring. Trace metal concentrations in environmental samples must be accurately determined to assess the toxic effects of these contaminants. The speed with which these analyses can be performed is an important factor in the selection of analytical methods since the effectiveness of environmental monitoring is lessened by elaborate, time-consuming analytical protocols.

Flame AAS has been widely employed for the analysis of trace metals in environmental samples. Despite the speed and accuracy of this method, significant errors result when AAS is applied to the analysis of samples such as sediment and soil that involve complicated matrices. This report presents methods for the detection and treatment of interferences resulting from matrix constituents in soil and sediment affected by the production and use of coal.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Reliable, cost-effective methods utilizing flame atomic absorption spectrophotometry (AAS) were developed for the trace elemental analysis of soil and sediment samples containing complex matrices. One matrix studied included aluminum and iron; the second matrix contained large concentrations of aluminum and iron plus lesser quantities of calcium, magnesium, manganese, phosphate, and potassium.

Conventional flame AAS methods produced accurate results for the analyses of cobalt, copper, lead, manganese, nickel, and zinc in these matrices. The barium, calcium, strontium, and vanadium content of these samples could not be accurately determined by conventional flame AAS techniques; however, reliable results were obtained using appropriate flame types with the addition of lanthanum and/or an easily ionizable alkali salt to all samples and standards. Interferences present in the analyses of beryllium, chromium, and titanium were difficult to correct for samples containing large concentrations of interfering matrix constituents. The use of matrix-matched standards was recommended for samples of this type. The analysis of selenium is commonly performed using a nitrous oxide-acetylene flame. However, the detection limit obtained using this technique may not be sufficient for most applications since small concentrations of selenium are very toxic. Direct AAS analysis of selenium using alternate flame types involved interferences that were not corrected by those techniques selected for investigation and were therefore beyond the scope of this research effort.

Procedures used in this research should be applicable to all environmental samples containing similar matrices. Information provided in this report will permit adaptation of these AAS techniques to samples other than those examined here.

Trace metal contamination is a major concern in many areas of environmental control other than coal production and consumption. Because environmental samples usually contain complicated matrices that vary widely in composition, the analysis of samples containing a large variety of matrix components should be investigated for a diverse number of trace elements. A broad knowledge of the control of interferences involved in the analysis of trace metals by AAS is essential for the accurate assessment of environmental abuse.

The analysis of arsenic and selenium in environmental samples is of particular importance; the extreme toxicity of these elements makes accurate detection of small concentrations imperative. Reliable methods of sufficient

sensitivity are not presently available for the analysis of arsenic and selenium by direct flame AAS. Alternative methods with adequate sensitivities are time consuming. More sensitive, time-saving methods should be sought for these analyses.

Investigation of methods of trace element extraction from soil and sediment samples was not within the scope of this research. However, the efficiency and reproducibility of the sample preparation procedure is essential to the reliability of the final result. Research in this area should be continued.

SECTION 3

SAMPLE COLLECTION

The samples acquired for this research were selected from two different environmental situations. One sample set consisted of bottom sediment affected by acid drainage from coal mines. The second group was soil samples subjected to exposure to fallout from a coal-fired power plant. Background samples were collected for each sampling site to assist in evaluation of the results.

SITE SELECTION

Sediment Affected by Acid Mine Drainage

Selection of a sampling site influenced by acid mine drainage was accomplished with the aid of the Region III Wheeling Field Office of the U.S. Environmental Protection Agency, Wheeling, West Virginia. The sampling operation was supervised by Roland W. Schrecongost, Director, and Scott C. McPhilliamy, Environmentalist.

The sampling program outlined in the proposal was modified to reduce the cost and effort required to obtain the samples. The Kiskiminetas was recommended as a potential primary river, with the Allegheny serving as a secondary stream. Mr. Schrecongost and his staff of the Wheeling Field Office evaluated this system and others applicable to the study. The Kiskiminetas River is a primary stream receiving nearly 26,000 kg (58,000 lb) of acid per day from coal mining activities. The Allegheny is of good water quality upstream of the Kiskiminetas and would serve as a suitable background area.

The second area evaluated for sampling was Toby Creek and the main stream Clarion River in Pennsylvania. Toby Creek qualifies as a primary stream since this stream is mineralized and acidic under all conditions. The quality of the Clarion River has deteriorated due to the influx of acid mine drainage from Toby Creek. The background sampling area for this system is the Clarion River above Toby Creek, which is only slightly affected by acid mine drainage. The Wheeling Field Office recommended selection of the Toby Creek/Clarion River water system since samples could be procured easily. Highway bridges, footbridges, and ponds exist along the waterways and would facilitate sampling at several points.

A total of 17 sample collection points was selected for the Toby

*All figures and tables mentioned in the text are included in Section 6.

Creek/Clarion River system. The map in Figure 1* specifies the location of these sites, which were sampled the week of June 14, 1976. A left bank sample, a right bank sample, and a midstream sample were taken at each site. The background samples are numbered 1 through 5, the primary stream samples are numbered 6 through 10, and the secondary stream samples, 11 through 17. The samples taken at site 13 did not include a midstream location since the bottom was solid rock. A list of sample designations and sampling locations is given in Table 1. The prefix "PA" (Pennsylvania) was added to each site number to simplify identification. U.S. Geological Survey topological maps showing the exact location of each sampling site were forwarded to Gulf South Research Institute by the EPA Wheeling Office. Specific locations for each of the 17 sampling sites are shown in Figures 2 through 8.

Soil Samples Affected by Coal Combustion

The second group of samples acquired represented soil exposed to the effects of coal combustion. Plant Jack Watson in Gulfport, Mississippi, is one of the few power plants in proximity to New Orleans that use coal as an energy source. GSRI contacted Southern Services Company, the parent company of the Mississippi Power Company, for permission to obtain the required number of soil samples. These efforts were aided by Larry D. McNair, the resident environmentalist for Southern Services, who was conducting a study at Plant Jack Watson. Mr. McNair offered to act as intermediary for GSRI and accompanied the GSRI sampling team to Plant Jack Watson.

The emission stack at the plant is 93 m (305 ft) high and is equipped with an electrostatic precipitator which, according to Mr. McNair, is very efficient. However, the dispersion pattern of fallout from the stack has not been determined, and the current study is not of sufficient magnitude to obtain information of this type.

A good indication of the geography of the land surrounding this power plant can be obtained from Figure 9, which is a reproduction of an infrared photograph.* The area on the eastern side of the plant is primarily marshland and would present the greatest sampling difficulty. In addition, the presence of a small number of housing developments on the east side indicates that the area has been disturbed and therefore is unsuitable for sampling. The area west of the plant is both industrialized and residential. Several industries, including a creosote plant, a weld-fabricating facility, and a chemical plant, are located in this vicinity. Because the soil samples preferred for this study are those that have not been affected by other industrial concerns, this area was also avoided.

Farmland and residences are located directly north of Plant Jack Watson. Interstate 10 lies approximately one-half mile north of the plant. The sampling site was chosen north of the interstate since this area is in proximity to the coal combustion process, is easily accessible to the sampling team, and is removed from the close-range effects of other industrial effluents. A topographic map illustrating the 14 selected sample sites and

*Maps and photograph supplied to GSRI through the courtesy of Mr. McNair of Southern Services Company.

Plant Jack Watson is presented as Figure 10.

Six additional samples of the same soil type were collected to provide background measurements for these 14 samples. Areas along Interstate 10 between Gulfport, Mississippi, and the Mississippi state line that were removed from industrial activity were selected as collection sites and are indicated on the map in Figure 11. The areas immediately adjacent to the interstate were not sampled since these areas are disturbed land masses. A complete list of the sampling locations for these 20 samples is given in Table 2. The prefix GP was used to indicate the samples were from the Gulfport sampling site.

COLLECTION OF SAMPLES

One-liter polyethylene wide-mouth jars with linerless caps were prepared for sample collection. The bottles were washed with detergent, thoroughly rinsed, and washed in 1:1 nitric acid and 1:1 hot hydrochloric acid. Each acid wash was followed by thorough rinsing with deionized, distilled water.

A total of 51 empty sample containers and 2 shipping blanks was sent to the Wheeling Field Office for the sediment (PA) sample collection. The shipping blanks were returned intact with the samples. The GSRI sampling team collected 20 soil samples from the Gulfport, Mississippi, area in identically cleaned containers and carried a designated shipping blank throughout the entire procedure.

SECTION 4

EXPERIMENTAL PROCEDURES

GLASSWARE CLEANING

All glassware used in sample preparation and analysis was washed with detergent, a solution of 1:1 nitric acid, and a hot solution of 1:1 hydrochloric acid. Each item was thoroughly rinsed between washings with deionized, distilled water. This rigorous cleaning procedure eliminated significant contamination from the glassware.

REAGENTS AND STANDARDS

All chemicals and reagents employed were of reagent grade or better. Standards used in AAS analyses were prepared daily from standard stock solutions (1000 ppm metal) purchased from Ventron Corporation, Beverly, Massachusetts. Sodium chloride and potassium chloride used throughout the study were recrystallized to remove trace metal contamination. Aluminum, calcium, magnesium, manganese, lanthanum, and phosphate used in the study of matrix interferences were obtained as the following compounds: $AlCl_3$, $CaCl_2 \cdot 2H_2O$, $MgCl_2$, $MnCl_2$, $La(NO_3)_3 \cdot 6H_2O$, and H_3PO_4.

APPARATUS

Atomic absorption spectrophometric analyses were performed using a Perkin-Elmer model 306 AAS instrument equipped with a Perkin-Elmer model 56 recorder. A 3-slot, 10-cm (4-inch) burner was employed for all analyses requiring an air-acetylene flame, except that for nickel analysis. A single-slot, 10-cm (4-inch) burner head was used for the nickel analysis. Those analyses utilizing a nitrous oxide-acetylene flame were performed with a conventional 5-cm (2-inch) nitrous oxide burner head. Flame conditions employed for the initial analyses of the sediment and soil samples were selected from the Perkin-Elmer AAS manual.[1]

SAMPLE PREPARATION

Preparation of the soils and sediments was initiated immediately upon receipt of the samples. All samples were thoroughly mixed to insure homogeneity. After mixing, the samples were dried to a constant weight in a 105°C oven so that results could be reported on a dry-weight basis. The samples were then ground in mortars, mixed again, and redried. These ground samples were transferred to sterile Whirlpack bags and refrigerated until needed for further sample preparation.

The partial digestion procedure recommended by EPA for analysis of sediments was selected for these analyses. Details of the procedure are provided in the Appendix. Experience with the analysis of soil and sediment led to the adoption of some modifications with the consent of EPA. During previous studies it was determined that 1 to 2 g of sample is insufficient to detect metals at very low levels.[2] Thus, a 4-g sample aliquot was employed, along with a final dilution volume of 50 ml to obtain lower detection limits. In order to effect efficient extraction of all metals, the aliquots of HCl and HNO_3 were increased to 10 and 1.0 ml, respectively, for use with 4-g aliquots[3]. The digestion period was increased to approximately 3 hours (the time required to reduce the volume to 10 to 15 ml). Past research has shown this procedure to provide increased recovery of copper, chromium, iron, nickel, and vanadium.[2]

Trace metal concentrations in the acid extracts obtained by the above procedure are stable for approximately 6 months. Consequently, aliquots of each sample had to be digested at three intervals during the contract period to provide sufficient sample extracts for accurate research. For convenience, a group of samples prepared at the same time will be referred to as a "set." A total of four sample sets was analyzed at appropriate times throughout the study. Sets I and II each contained extracts of both the soil and sediment samples. Set III contained only extracts of the soil samples, and Set IV included only extracts of the sediment samples.

QUALITY CONTROL

A reagent/glassware blank was included with each of the four analysis sets. A single shipping blank for the soil samples and two shipping blanks for the bottom sediment samples were carried throughout the sampling procedures and were analyzed for contamination along with the analysis of Set I. Three duplicates and three spiked soil and sediment samples were included in analysis Set III. Four duplicates and three spiked sediment samples were in analysis Set IV.

Because standard reference materials for soil and sediment analysis were not available from the National Bureau of Standards, two sediment pools were used in this study for in-house reference sediments. These two sediment pools were referred to as reference sediments B and C. Replicates and spiked aliquots of each of these sediments were included in analysis Sets II, III, and IV.

SECTION 5

RESULTS AND DISCUSSION

The analyses of trace elements and major inorganic constituents in soil and sediment samples were initially performed by flame AAS using analytical conditions recommended in the Perkin-Elmer AAS analytical manual.[1] The objective of this research was to develop interference-free flame AAS techniques for the analyses of the trace elements detected. These initial analyses were therefore investigated for possible interferences and for ways to eliminate the interferences. The analyses of the detectable trace elements in the soil and sediment samples were finally performed again by AAS using the analytical conditions subject to the least interference. The flow chart in Figure 12 outlines the scheme of this research. The research is detailed below in four sections: initial analyses, interference study, final analyses, and quality control procedures.

INITIAL ANALYSES

A list of trace elements of environmental interest and major constituents for each sample set was compiled with the aid of published literature and past experience in the study of these interferences. The major inorganic elements for both sets of samples were aluminum, calcium, iron, magnesium, potassium, phosphate, and sodium. The trace metals examined differed for the soil (GP) and bottom sediment (PA) samples. The soil samples were examined for trace constituents present in fallout from coal-fired power plants.[3] The bottom sediment samples were analyzed for trace metal contaminants arising from acid mine drainage.[4] The trace elements studied in the soil samples include antimony, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, lead, nickel, selenium, silver, tin, titanium, and zinc. The bottom sediments were analyzed for barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, silver, strontium, vanadium, and zinc.

All constituents except phosphate were analyzed by flame AAS and calibrated using aqueous standards. The conditions employed for each of these analyses are detailed in Table 3. Phosphate was analyzed by the phosphomolybdovanadate colorimetric method measuring the intensity of the yellow color at 470 nm.[5] The interference from ferric ion was corrected for by using an aliquot of the sample solution as a blank.

Soil Samples

The results of the analysis of the suspected major constituents in soil samples are displayed in Table 4. The matrix of the soil samples was less

complicated than that for the bottom sediment samples. Calcium, magnesium, sodium, and potassium were present in trace quantities; only aluminum, iron, and phosphate were considered as possible interferences for this sample set.

The trace metals analyzed are listed in Table 5. Of the 15 elements examined, the following nine were present in less than detectable concentrations: antimony, arsenic, beryllium, bismuth, cadmium, cobalt, lead, nickel, and tin. Those elements that were examined for the presence of interferences in the AAS analysis were calcium, chromium, copper, lead, magnesium, selenium, titanium, and zinc.

Bottom Sediment Samples

The concentrations of major inorganic constituents found in the bottom sediment samples (Table 6) varied greatly from sample to sample. However, aluminum, calcium, iron, potassium, magnesium, and phosphate were present in concentrations large enough to exert interferences in the analysis of trace elements. Calcium levels as low as 3.0 ppm were also observed. Calcium analysis was known to be subject to various interferences, especially to phosphate interference, and was investigated further in the study.

Table 7 contains lists of the concentrations of the suspected trace elements in the bottom sediment samples. Manganese was present in large enough concentrations to be considered a matrix element but was also examined for possible interferences. Cadmium, molybdenum, and silver were not detected in these samples. The hydrochloric acid used in the digestion procedure should have precipitated silver (if any) as silver chloride in the digestate. Those elements in the sediment samples that were selected to be examined for the presence of interferences are barium, beryllium, calcium, chromium, cobalt, copper, lead, manganese, nickel, strontium, vanadium, and zinc.

INTERFERENCE STUDY

The interferences in AAS analysis are typically of four types: chemical, ionization, spectral, and matrix. Except for the spectral interferences, these interferences can be detected using the method of standard additions (MSA) and/or extensive synthetic sample study. To minimize spectral interferences, a single-element lamp was used for all the analyses; deuterium background correction was employed for all applicable analyses.

Analysis by MSA involves preparation of a series of solutions, each containing an aliquot of a sample digestate. One of the solutions contains only the diluted digestate, whereas the remaining solutions also contain increasing concentrations of the trace element of interest. The solutions are analyzed by flame AAS along with a series of aqueous standards. The peak heights obtained from the analysis are plotted on the y-axis of a graph (using linear regression analysis), and the known additions are plotted on the x-axis. The x-intercept of the MSA plot is used to calculate the unknown concentration in the sample as shown in Equation 1.

$$\text{ppm in sample} = \frac{(\text{x-intercept}) \times (\text{MSA dilution factor}) \times (\text{initial dilution vol.})}{\text{weight of sample used (g)}} \quad (1)$$

Only the solutions or standards that produced absorbances in the linear range of an analysis were used in order to maintain the validity of the aqueous or MSA results. Any curve having a correlation coefficient of less than 0.999, if suspected to be due to experimental error, was discarded and the experiment repeated.

Sample digestates analyzed by MSA are diluted during the process of an MSA experiment. This dilution reduces the concentrations of the matrix constituents and thereby reduces possible interferences. An effort was made to minimize the sample dilutions while maintaining all the MSA solutions in the linear range.

Because MSA alone does not identify the interferences in AAS analyses,[6] synthetic sample studies were performed. The synthetic samples are solutions containing specific concentrations of one or more matrix constituents along with the trace element of interest. The concentration of that trace element in these solutions represents the average concentration in the sediment or soil sample extracts. Deionized, distilled water was used to prepare a reference solution that contained only the trace element. The effect of the added constituent is indicated by the percent net change in peak height calculated as:

$$\% \text{ net change} = \frac{\text{peak ht(with interference)-peak ht(without interference)}}{\text{peak ht(without interference)}} \times 100 \quad (2)$$

Interference studies for trace elements of interest are detailed below in alphabetical order.

Arsenic

Direct AAS analysis of soil sample extracts for arsenic using a nitrous oxide-acetylene flame yielded a detection limit of 37 ppm. No arsenic was detected in any of the GP samples using this method of analysis. Each sample was reanalyzed for arsenic using an argon-hydrogen flame with a wavelength of 193.7 nm and a spectral band width of 0.7 nm. The results indicated that all samples contained less than the detection limit of 6 ppm arsenic (on a dry-weight basis); therefore, analysis for arsenic was not pursued.

Later research efforts focused on the analysis of selenium showed that serious interferences were inherent in the use of argon-hydrogen flame, mostly due to its relatively low temperature. Alternate analysis methods capable of detection of low arsenic concentrations, i.e., hydride generation and flameless AAS, are beyond the scope of this research (p. 17).

Barium

Barium was determined using a wavelength of 553.6 nm, a spectral band width of 0.4 nm, and a nitrous oxide-acetylene flame. A concentration of 0.2 percent potassium or sodium salt (recrystallized from reagent grade KCl or NaCl) was added to all test solutions. Calcium has been reported to elevate the barium result in AAS analysis because the undissociated CaOH in the flame absorbs at the barium wavelength (554 nm).[7-9] Figure 13 shows the

MSA curves of 3 samples containing different amounts of calcium in the digestate: PA-3 (28 ppm Ca),* PA-6 (127 ppm Ca), and PA-12 (1236 ppm Ca). The graph suggests additional interferences that cannot be assigned to the presence of calcium since the aqueous calibrated results were less than the MSA results. An examination of the sources of this depression can be made from the synthetic sample study in Table 8. Aluminum, at a concentration of 500 ppm, depressed the absorbance of barium by 36 percent. A 10 percent depression was caused by the presence of iron at a concentration of 5000 ppm. The remaining constituents, when added at the same high level, showed only slight effects at the concentrations present in the sediment sample digestates.

In an attempt to control interferences from aluminum and iron, a second set of synthetic samples containing 0.2 percent lanthanum (as La_2O_3) was analyzed. The results shown in Table 9 indicate that lanthanum is very effective in controlling these interferences when used in conjunction with an alkali metal salt. A concentration of 500 ppm aluminum depressed the absorbance of 5 ppm barium by 5 percent under these conditions. The barium peak height was suppressed only 5 percent by a concentration of 5000 ppm iron. A concentration of 50 ppm calcium, magnesium, or manganese produced insignificant effects. The effect of phosphate was also studied under these conditions and was determined to be inconsequential.

The ability of lanthanum to reduce interferences effectively was substantiated by the following experiments. Digestates of sample PA-3 and PA-12 were each subjected to two analyses by MSA. With the addition of only potassium to the samples and standards in the first MSA analysis (Figure 14), the barium absorbances were depressed. The analysis was repeated with a concentration of 0.2 percent lanthanum also added. The interferences were minimal with both potassium and lanthanum added, as shown in Figure 15.

It was concluded that the barium analysis of soil and sediment sample digestates was most accurate when performed using a nitrous oxide-acetylene flame with a concentration of 0.2 percent lanthanum and potassium (or sodium) added to all samples and standards.

Beryllium

Beryllium was analyzed with a nitrous oxide-acetylene flame, using a wavelength of 234.9 nm and a spectral band width of 0.7 nm. The MSA analysis of sample PA-16, as shown in Figure 16, exhibited a depressed beryllium absorbance. A set of synthetic samples was analyzed to determine the source of the depression. The data in Table 10 indicate a severe interference from aluminum. The effects of iron, magnesium, and manganese were insignificant at concentrations present in the sediment samples.

Fleet et al. reported that 2.5 percent oxine (8-hydroxyquinoline) was effective in controlling the interference of 4000 ppm aluminum on 4 ppm beryllium.[10] Table 11 contains the data from a brief study of the potential

*Concentration of calcium in sample digestate.

for oxine (at less than 2.5 percent) to reduce the interference of 400 ppm aluminum. The amount of oxine added did not significantly alter the effect of aluminum. To attain 2.5 percent oxine in a given test solution, it is necessary to dilute the acid digestates by a factor of 2 since 5 percent oxine* was used for the addition. The beryllium concentrations in these digestates were very near the detection limit of the instrument; therefore, dilution of these digestates was not possible.

Table 12 contains additional data for the analysis of beryllium. Calcium and phosphate had no significant effect on the absorbance of beryllium, and the addition of 0.1 percent lanthanum did not correct the interference caused by the presence of aluminum.

An attempt was made to analyze the sediment sample digestates for beryllium using matrix-matched standards. The average concentration of each PA matrix constituent determined was added to the standard solutions. However, because less than 0.2 ppm beryllium was present in the sample digestates, the difference in the beryllium results obtained from the matrix-matched standards compared to those of the aqueous standards was no more than 0.02 ppm in the digestates. The present study was unable to treat such a small variation adequately. The use of matrix-matched standards would be necessary to analyze samples containing larger beryllium concentrations. Alternate methods of controlling the interference due to aluminum should also be investigated.

Calcium

A wavelength of 422.7 nm and a spectral band width of 1.4 nm were used for the analysis of calcium. An air-acetylene flame with 0.2 percent sodium (as NaCl) added to the test solutions was used to analyze samples PA-7 and GP-1 by MSA. Extreme depression was indicated by the resultant MSA graphs, as displayed in Figures 17 and 18.

Lanthanum concentrations of 0.1 to 1 percent were reported to provide effective control of the interferences of the calcium analysis in the air-acetylene flame.[11] The following experiment was designed to determine the optimum amount of lanthanum needed for controlling the interferences. Aliquots of the digestate from sample PA-1, diluted by a factor of 25, were treated with increasing concentrations of lanthanum. The AAS results are illustrated in Figure 19. The enhancement in absorbance was maximized by the addition of 0.2 percent lanthanum; however, the enhancement was decreased with the addition of more than 0.2 percent lanthanum.

The capability of 0.2 percent lanthanum to reduce interferences in the air-acetylene flame was tested with the use of synthetic samples. Table 13 shows the individual effects of aluminum, iron, magnesium, manganese, and phospate on the absorbance of 5 ppm calcium. A concentration of 0.2

*Five percent oxine dissolved in hydrochloric acid was prepared; precipitation resulted when more oxine was added, although Fleet et al. reported the dissolution of 10 percent oxine.

percent lanthanum and 0.2 percent sodium was added to all solutions. The effect of aluminum on the absorbance of calcium was drastically reduced, and the effects of iron, magnesium, manganese, and phosphate were minimal.

Because most AAS analyses using a nitrous oxide-acetylene (hotter) flame are subject to fewer interferences than those using an air-acetylene flame, calcium analysis using nitrous oxide-acetylene was also investigated. However, even with 0. 2 percent sodium added to all solutions, strong depression of the calcium absorbance was indicated by the MSA graphs for digestates of samples GP-7 and PA-1, shown in Figures 20 and 21. The depression was not as serious as that initially encountered using the air-acetylene flame.

A synthetic study was devised to identify the sources of the interference under the nitrous oxide-acetylene flame conditions. Table 14 presents a list of the individual effects of aluminum, iron, magnesium, manganese, and phosphate on the absorbance of calcium. Aluminum created the most serious interference; the remaining elements had little or no effect on the analysis of calcium.

The addition of lanthanum along with sodium to the digestate of sample PA-1 was used to investigate the interferences in the nitrous oxide-acetylene flame. The results of this study, shown in Figure 22, indicate that the addition of lanthanum enhanced the calcium absorbance, and that any addition of lanthanum in concentrations between 0.2 and 2.0 percent produced comparable results. This phenomenon is especially significant since the calcium absorbance with the air-acetylene flame was more critically dependent on the concentration of lanthanum added.

Another synthetic sample study was performed with a nitrous oxide-acetylene flame with a concentration of 0.2 percent lanthanum and 0.2 percent sodium added to all solutions. The results shown in Table 15 indicate that none of the added constituents had any significant effect on the absorbance of 5 ppm calcium.

Calcium results of MSA analyses for four samples, with and without lanthanum, using both air-acetylene and nitrous oxide-acetylene flame are provided in Table 16. With both sodium and lanthanum added, each of the flame types yielded similar MSA and aqueous (aq.) calibrated results, as shown in Figures 23 through 26. However, the nitrous oxide-acetylene flame was used for the final analysis since it is subject to less interference, as shown by the synthetic sample study.

Chromium

The wavelength used for chromium determinations was 357.4 nm with a spectral band width of 0.7 nm. A nitrous oxide-acetylene flame was used since the chromium analysis with an air-acetylene flame is subject to interferences from iron and nickel.[1] The existence of interferences in the chromium analysis with a nitrous oxide-acetylene flame was indicated by the nonparallel relationship of the aqueous and MSA curves for sample GP-10 shown in Figure 27. Very slight interference was indicated by the MSA for sample PA-13, as shown in Figure 28. This interference was substantiated by

the synthetic sample study summarized in Table 17, which represents the effects of aluminum, calcium, iron, potassium, magnesium, manganese, and phosphate on chromium absorbance. Nickel, a known interference for chromium analysis, was not included since it was present only in trace quantities. The results of the synthetic sample study had been corrected for the chromium absorbance exhibited by the iron solutions used for making up the synthetic samples. The significant increases in the chromium absorbance observed for each of the constituents added suggested an ionization interference.

To control the ionization interferences, a concentration of 0.2 percent sodium (as NaCl) was added to the same set of synthetic samples. The results, listed in Table 18, showed considerably fewer interferences. The only added constituent that still produced any significant effect was iron. The average iron concentration in the bottom sediment digestates was 5000 ppm; this concentration decreased the absorbance of 3 ppm chromium by 6 percent. To remove the iron interference from the chromium analysis, 1 percent lanthanum (as $LaCl_3 \cdot 6H_2O$), along with 0.2 percent sodium (as NaCl), was added to all solutions. The results of the synthetic sample study thus obtained were identical to those of the previous study (Table 18) without the addition of lanthanum. Moreover, the MSA graphs for the digestate of sample PA-17 with and without lanthanum added were nearly identical, as shown in Figure 29, whereas both were parallel with the aqueous standard curve. This study indicated that the addition of 1 percent lanthanum did not affect the analysis of chromium in the presence of 0.2 percent alkali metal salt.

Background absorbance was suspected both in the synthetic solutions and in samples containing high iron concentrations since the solution of 1 percent $FeCl_3$ used for the preparation of synthetic samples showed an absorbance equivalent to that of 1.3 ppm chromium. This suspicion was tested using a uranium lamp, since the principal resonance line of uranium (358.5 nm) is close to that of chromium (357.9 nm) and serves as a non-absorbing wavelength. No significant background absorbance was detected either in the 1 percent iron solution or any of the soil or sediment sample digestates. This study indicated that the chromium analyses of the soil and sediment samples are not subject to any serious interferences using a nitrous oxide-acetylene flame with 0.2 percent sodium added to all solutions. However, samples containing greater concentrations of iron may require matrix-matched standards or other techniques for controlling the interference caused by iron.

During the final performance of this research, an article about chromium analysis submitted by Rawa and Henn appeared in the August 1977 issue of American Laboratory.[12] This article reported that a nitrous oxide-acetylene flame was preferred to the air-acetylene flame for chromium analysis, and that the chromium analysis using an air-acetylene flame is subject to certain interferences even with 1 percent oxine added to all test solutions. However, the present study shows that chromium analysis with nitrous oxide-acetylene is not entirely interference free, and that the ionization of chromium in the flame is sufficiently serious to require corrective measures.

Cobalt

The analysis of cobalt was performed with an air-acetylene flame using a wavelength of 240.7 nm with a spectral band width of 0.2 nm. The MSA plot in Figure 30 indicates a very slight depression of the aqueous calibrated results. Two sets of synthetic samples were prepared to examine possible sources of interference in the cobalt analysis. The first set (Table 19) indicated no interference from aluminum, iron, potassium, magnesium, or manganese; the second set (Table 20) indicated no interference from calcium or phosphate. Because this interference was insignificant, further research was not performed for cobalt.

Copper

Copper was analyzed with an air-acetylene flame at a wavelength of 324.8 nm with a spectral band width of 0.7 nm. The MSA plots for samples GP-4 and PA-5, as shown in Figures 31 and 32, were nearly parallel with the aqueous standard curve. Because past studies by GSRI (Table 21) have shown that copper is relatively free from iron and aluminum interferences in the soil and sediment matrices, no further studies were conducted.[2]

Lead

The AAS analysis of lead was performed using an air-acetylene flame, a wavelength of 283.3 nm, and a spectral band width of 0.7 nm. A graph of the MSA and aqueous curves for digestates of sample GP-5 (Figure 33) indicate a slight elevation of the lead absorbances in the sample. The same effect is apparent for sample PA-14 (Figure 34). Although the interferences are slight, the analysis of lead was investigated further using synthetic samples. The data obtained from the synthetic sample study are displayed in Table 22. None of the added constituents produced an appreciable effect on the analysis of 5 ppm lead. A combination of excessive amounts of all these constituents proved to produce insignificant changes in the lead absorbance. The use of synthetic samples showed that the analysis of lead in these soil and sediment samples was not subject to significant interferences.

Magnesium

The magnesium analyses were performed with a nitrous oxide-acetylene flame, using a wavelength of 285.2 nm and a spectral band width of 0.7 nm. Magnesium concentrations in the soil samples were large enough to permit the dilution of the GP-5 digestate by a factor of 100 for analysis by MSA. The graph in Figure 35 displays excellent correlation between the MSA and aqueous standard curves for sample GP-5. The analysis of magnesium was not affected by the aluminum and iron concentrations present in the soil and sediment digestates.

Manganese

An air-acetylene flame, a wavelength of 279.5 nm, and a spectral band width of 0.2 nm were the conditions used for manganese analyses. Figure 36 illustrates the MSA plot for PA-14 (diluted by a factor of 100). The near-

parallel lines in the graph represent the minimal interference encountered in this analysis. The content of manganese obtained for sample PA-4 by MSA was 502 ppm; the value obtained by aqueous calibration was 498 ppm. No further study was deemed necessary for manganese.

Nickel

An air-acetylene flame was used for nickel analysis; a wavelength of 232.0 nm with a spectral band width of 0.2 nm was selected. The digestate of sample PA-2 was analyzed by MSA and was diluted by a factor of 3. The resultant MSA plot in Figure 37 indicates no significant interference for the nickel analysis. Therefore, the AAS conditions used here were used for the final analysis of nickel in these digestates.

Selenium

The wavelength for selenium analyses was 196.0 nm with a spectral band width of 0.7 nm. An argon-hydrogen flame was selected for the initial analysis of selenium because the low selenium concentration in the soil sample digestates could not be detected by direct AAS analysis using either an air-acetylene flame or a nitrous oxide-acetylene flame.[13,14] However, Figure 38 depicts the severe depression of selenium absorbance exhibited by an MSA study of sample GP-9. The value obtained by MSA (14.1 ppm) was significantly greater than that obtained by aqueous calibration of the undiluted digestate (5.1 ppm).

The sources of the interferences were studied using synthetic samples containing aluminum, calcium, iron, potassium, and magnesium. The severe depressive effects of these constituents (except potassium) are readily observed in Table 23. Aluminum produced the strongest effect by depressing the selenium peak height by more than 90 percent. A concentration of 25 ppm aluminum produced approximately the same effect as 1000 ppm aluminum. The iron concentrations tested ranged from 50 to 1000 ppm, and the resulting depressions ranged from 50 to 76 percent. The presence of potassium in concentrations ranging from 50 to 500 ppm produced negative effects ranging from 1 to 7 percent.

Methods employed to alleviate the aluminum interferences, including various additions of EDTA, disodium EDTA, sodium, or lanthanum, are outlined in Table 24. None of the additives resulted in effective removal of the interference; addition of lanthanum caused major depression of the selenium absorbance.

Three spiked soil samples were examined using three flame types: argon-hydrogen, air-acetylene, and nitrous oxide-acetylene. These soil samples, each containing less than 14 ppm selenium, were spiked with 50 ppm selenium. The results for the analyses of these spiked samples are listed in Table 25. The concentration of selenium in all three spiked samples should be in the range of 50 to 64 ppm. However, the values obtained were less than 30 ppm selenium with an argon-hydrogen flame, more than 64 ppm selenium with a air-acetylene flame, and 55 ppm for all three samples with a nitrous oxide-acetylene flame.

The experiment described above showed that although the selenium analysis with the argon-hydrogen flame was subject to negative interferences because of the relatively cool flame temperature, the analysis with the air-acetylene flame is subject to positive interferences. The analysis using a nitrous oxide-acetylene flame appears to be the most accurate of the three; however, this method has a minimum detection limit of 25 ppm. Neither the use of an air-acetylene flame nor that of a nitrous oxide-acetylene flame was investigated further since selenium in these soil samples was not detectable in either flame system.

The method most often used for the analysis of low selenium concentrations is either the flameless AAS or the hydride-generation method using an argon-hydrogen flame atomization.[15-18] These methods were not within the scope of work and were not investigated further. However, it has been reported by Pierce and Brown that interferences are present for selenium analysis by these two methods, and that an automated hydride generation method using a quartz tube for atomization is subject to the least interference.[18]

Strontium

A wavelength of 460.7 nm and a spectral band width of 1.4 nm were used for all strontium analyses. In the initial analyses of strontium, a nitrous oxide-acetylene flame was used and 0.2 percent potassium (as KCl) was added to all test solutions to control interferences from ionization in the flame. The MSA experiment for sample PA-7, as shown by the nonparallel lines in Figure 39, indicates the presence of interferences. The strontium content in sample PA-7 was determined to be 15.0 ppm from aqueous calibration and 20.7 ppm from MSA.

Synthetic samples were used to investigate interferences encountered in the initial analysis of strontium with 0.2 percent potassium added to all samples and standards. The results are listed in Table 26. The only added constituent that caused severe interference was aluminum; a concentration of 500 ppm aluminum depressed the strontium absorbance by 25 percent.

To minimize the interference due to aluminum, a concentration of 1 percent lanthanum as $La(NO_3)_3 \cdot 6H_2O$ was added to the set of synthetic samples containing 0.2 percent potassium as KCl. The results in Table 27 reveal a considerable improvement. At concentrations present in the sediment matrix, aluminum, iron, manganese, and phosphate have only minimal effects on the absorbance of strontium. In this study, phosphate concentrations of 200 ppm and 500 ppm caused considerable baseline noise and a depressive effect for the strontium absorbance. These effects were due to the aspiration of the precipitate of lanthanum phosphate into the flame. Filtration should remove the precipitate and thus the interference; it has been reported that strontium was not removed by the filtration process.[19]

The accuracy of the analysis using a nitrous oxide-acetylene flame with 1 percent lanthanum and 0.2 percent sodium in all solutions was substantiated with analysis by MSA. Figure 40 and Figure 41 show the MSA plots for digestates of samples PA-14-sp (sample PA-14 spiked with 50 ppm strontium) and PA-15, with and without lanthanum added. The interference observed

without lanthanum added (Figure 40) disappeared when lanthanum was added (Figure 41).

The strontium analysis using an air-acetylene flame with addition of both lanthanum and sodium to all test solutions was also investigated, since this method was suggested in the Perkin-Elmer AAS Users Manual.[1] The MSA analyses of digestates of samples PA-14-sp and PA-15 utilizing these conditions are shown in Figure 42. Both MSA plots revealed interferences in the analysis of strontium.

Synthetic samples were used to study the sources of the interference in the air-acetylene flame including both sodium and lanthanum addition. The data in Table 28 indicate that iron and magnesium have a significant negative effect on the absorbance of 2 ppm strontium. This technique is not suitable for analysis of these soil and sediment samples.

The strontium concentrations in samples PA-14-sp and PA-15 as obtained by aqueous calibration and MSA utilizing different flame types and conditions are listed in Table 29. Only the strontium analysis performed in a nitrous oxide-acetylene flame with both sodium and lanthanum added yielded aqueous calibrated results similar to the MSA results, and this method was used for the final analyses.

Titanium

The analysis of titanium was performed with a nitrous oxide-acetylene flame; a concentration of 0.2 percent sodium (as NaCl) was added to all test solutions. A wavelength of 365.3 nm with a spectral band width of 0.2 nm was selected for this determination.

The MSA experiment for the sample GP-10 digestate (dilution factor of 2), shows a very slight interference in the titanium analysis (Figure 43). The concentration of titanium in sample GP-10 was 118 ppm by the aqueous standard calibration curve and 122 ppm by MSA.

A synthetic sample study was performed to search for interferences not readily observable in the MSA study. As listed in Table 30, the presence of calcium, iron, and phosphate all produce slightly negative effects on the absorbance of 30 ppm titanium in the presence of sodium. A concentration of 500 ppm aluminum produced a 7 percent increase of the titanium peak height. A solution containing average quantities of matrix constituents present in soil digestates showed a 7 percent elevation of the titanium results.

In an effort to eliminate the interferences produced by aluminum, calcium, and iron, a second synthetic sample study was performed with 1 percent lanthanum as $La(NO_3)_3 \cdot 6H_2O$ added to all solutions. Rather than lessening the degree of interference, the negative interferences were enhanced, as shown in Table 31. This effect was also observed in the MSA plot of GP-10 (Figure 44). With both lanthanum and sodium added, the calculated titanium content in sample GP-10 was 52 ppm using the aqueous calibration curve and 130 ppm as determined by MSA experiments. The addition of lanthanum is detrimental rather than helpful for the analysis of titanium.

Because the analysis of titanium using a nitrous oxide-acetylene flame with a concentration of 0.2 percent sodium added to all solutions was subject to some interferences, matrix-matched standards were used for the final analyses of titanium in the soil samples.

Vanadium

For all the vanadium analyses, a nitrous oxide-acetylene flame was employed, using a wavelength of 318.4 nm with a spectral band width of 0.7 nm. Interference in the vanadium analysis was obvious from the MSA plot for sample PA-15 shown in Figure 45. The concentration of vanadium in PA-15 was 33 ppm from the aqueous standard curve and 24 ppm from the MSA experiment.

The synthetic sample study, shown in Table 32, represents the effects of aluminum, calcium, iron, potassium, magnesium, manganese, and phosphate on the absorbance of 6 ppm vanadium. At the average concentrations present in the sediment sample digestates, only manganese did not exhibit a substantial effect on the vanadium absorbance. The most surprising effect was that a concentration of 50 ppm potassium elevated the vanadium absorbance by 24 percent, and concentrations of 500 ppm potassium caused an increase of 36 percent in the vanadium peak height. This phenomenon indicated that vanadium may have been ionized in the flame and that the addition of potassium chloride (or any other alkali metal salt) should alleviate this interference.

A second analysis using synthetic samples with sodium added confirmed this suspicion. A concentration of 0.2 percent sodium (as NaCl) was added to all solutions listed in Table 33. As a result, all interferences were minimized except those due to iron. A 5000 ppm iron concentration, in the presence of sodium, decreased the vanadium absorbance by 17 percent. However, the effect of a combination of the six constituents was only 4 percent.

The experimental attempt for eliminating the interference caused by iron led to a vanadium study using the addition of 1 percent lanthanum along with 0.2 percent sodium. The results displayed in Table 34 show that the interferences due to aluminum, calcium, and even iron disappeared.

The MSA plots for sample PA-17 in the presence of sodium, with and without lanthanum added, were almost parallel with the aqueous standard curve as shown in Figure 46 and Figure 47. Results obtained for vanadium in the sample are similar and are listed in Table 35.

It has been reported by Zander that iron has a resonance line at 318.3 nm, which is very close to the wavelength used for vanadium analysis (318.4 nm).[20] The fact that no absorbance was observed for a 1 percent iron solution in the vanadium analysis at 318.4 nm indicates that the 318.3 nm is a very weak resonance line of iron. However, this spectral interference should be investigated if larger iron concentrations are present in the sample digestates.

Zinc

The analysis of zinc was studied using an air-acetylene flame, a wavelength of 213.9 nm, and a spectral band width of 0.7 nm. The MSA plot for soil sample GP-7, as displayed in Figure 48, shows a parallel relationship between the MSA and aqueous standard curves. The MSA analysis of sediment sample PA-7 is represented in Figure 49. The sample digestate was diluted by a factor of 50, and insignificant interferences were indicated by the results. Because zinc was not a trace metal of interest for these samples, and no significant interferences were observed, it was concluded that the zinc analysis with the air-acetylene flame was interference free.

FINAL ANALYSES

From the information gathered in the interference study, a list of the methods recommended for each element studied was compiled. This list is presented in Table 36. In the initial analyses of soil and sediment samples, the elements subject to interferences were: barium, beryllium, calcium, chromium, selenium, strontium, titanium, and vanadium. These and other elements were analyzed again using the methods given in Table 36 for the soil and sediment samples. Results of calcium analysis employing the recommended method listed in Table 36 yielded values different from those of the initial analysis. The calcium results for soil and sediment samples are listed in Table 37.

The results of trace elements for this final analysis are listed in Table 38 for soil samples and in Table 39 for bottom sediment samples. The following elements were present in concentrations less than the detection limit and were not included in the table: antimony, arsenic, bismuth, cadmium, selenium, and tin. All these results except that for titanium were calibrated against aqueous standards. Because the titanium analysis was subject to interferences, matrix-matched standards containing the average matrix concentration of the soil digestates were used for calibration. The aqeuous calibrated titanium results were also listed for comparison.

Although the interferences persist for the beryllium analysis, only the aqueous calibrated values were listed in the table because the low beryllium concentration in these samples (<2 ppm beryllium, dry-weight basis) resulted in a very slight difference (<0.2 ppm beryllium, dry-weight basis) between the values calibrated against aqueous and matrix-matched standard curves.

Because partial digestion procedures were used for this study, the resultant elemental contents in the soil and sediment samples represent only the hot acid extractable amount rather than the total amount of the element in the sample.

QUALITY CONTROL PROCEDURES

Quality assurance measures were employed throughout the project to ensure the validity of all data. The quality control procedures involved the analysis of shipping and reagent/glassware blanks to account for possible contamination during handling or preparation. Duplicate and spiked

samples and in-house reference sediments were included to confirm the accuracy and precision of the digestions and analyses.

Shipping Blanks

Designated shipping blanks accompanied the soil and sediment sample containers throughout the sampling process. The blanks were treated identically to the sample bottles except that these containers were returned empty and intact. The single shipping blank that accompanied the soil samples and the two shipping blanks for the sediment samples were tested for contamination by rinsing the containers with nitric acid and analyzing the extract by AAS. Results of these analyses are given in Table 40 as micrograms of the element of interest extracted from inside the sample container. Of the 24 elements tested, 15 were not detectable in the blanks. The remaining nine elements were detectable in the containers but could not contribute significantly to the elemental concentration in the sample since a minimum of 500 g of sample was collected in every bottle.

Soil and Sediment Samples

Duplicate Samples--

The results of duplicate analyses of the sediment and soil samples are an indication of both the homogeneity of the sample and the reproducibility of the digestions and analyses. Homogenization of the sediment samples was hindered by the presence of many small pebbles and rocks. The average value and standard deviation for each pair of duplicate samples displayed in Table 41 indicate good reproducibility. The methods of analysis used for sets III and IV are the same as those employed for the final analysis of the samples (Table 36).

Spiked Samples--

The metal concentrations selected for spiking the samples varied for each metal and were tailored to the metal concentrations present in the sample. The percent recovery for each of these spikes is listed in Table 42. Very good accuracy for this digestion procedure is generally indicated by these results. The AAS analysis procedures for each of these determinations are the same as those used for the analysis of the duplicate samples.

In-House Reference Sediments

Two sediments pools, reference sediments B and C, which had been prepared and analyzed previously by GSRI for seven of the trace metals of interest were used as in-house reference sediments.[21] Replicate and spiked aliquots of each of these sediments were digested and analyzed along with sets II, III, and IV. Set II was analyzed using the AAS conditions for initial analysis (Table 3). Sets III and IV were analyzed using the AAS conditions for final analysis (Table 36).

Replicate Samples--

Lists of the replicate values obtained for reference sediments B and C are summarized in Tables 43 and 44. The mean and standard deviation for these analyses were not calculated since improved methods of analysis were used for Sets III and IV. Reproducibility in Sets III and IV was excellent for most metals except titanium. The results for titanium in reference sediment C range from 15 to 122 ppm. Although the analysis method used for the titanium determination does suffer some interference, such a big discrepancy in the replicate results is probably the result of anomalies not defined in these experiments.

Quality control charts for reference sediments B and C are contained in Figures 50-62 for the following metals: barium, chromium, copper, lead, nickel, vanadium, and zinc. The values obtained during this research project are indicated by circles. The means and standard deviations from the previous project are indicated by the solid and dashed horizontal lines.[21] Results obtained for the analysis of barium, chromium, and vanadium in Sets III and IV were not necessarily expected to be comparable with the results from the previous project, since more accurate methods were used for the analysis of Sets III and IV. This difference is especially noticeable for the chromium analysis in reference sediment B (Figure 51). Using the same analysis method as that for the previous project, similar values were obtained (Set II); using the improved analysis method, lower values were obtained (Sets III and IV). The overall comparisons for most metals are favorable, except that for copper in reference sediment C (Figure 58). The present study showed a better precision than the previous one. Quality control charts to be used in the future based on these data will be modified to include the average and standard deviation values calculated using methods developed for this study.

Spiked Samples--

The percent recovery data are listed in Tables 45 and 46 for reference sediments B and C. Recoveries for most metals were very good, except for chromium, strontium, and vanadium in Set II, where improved analysis methods were used and earlier values were probably inaccurate. Percent recoveries for titanium were not calculated because the replicate samples gave inconsistent results.

SECTION 6

FIGURES AND TABLES

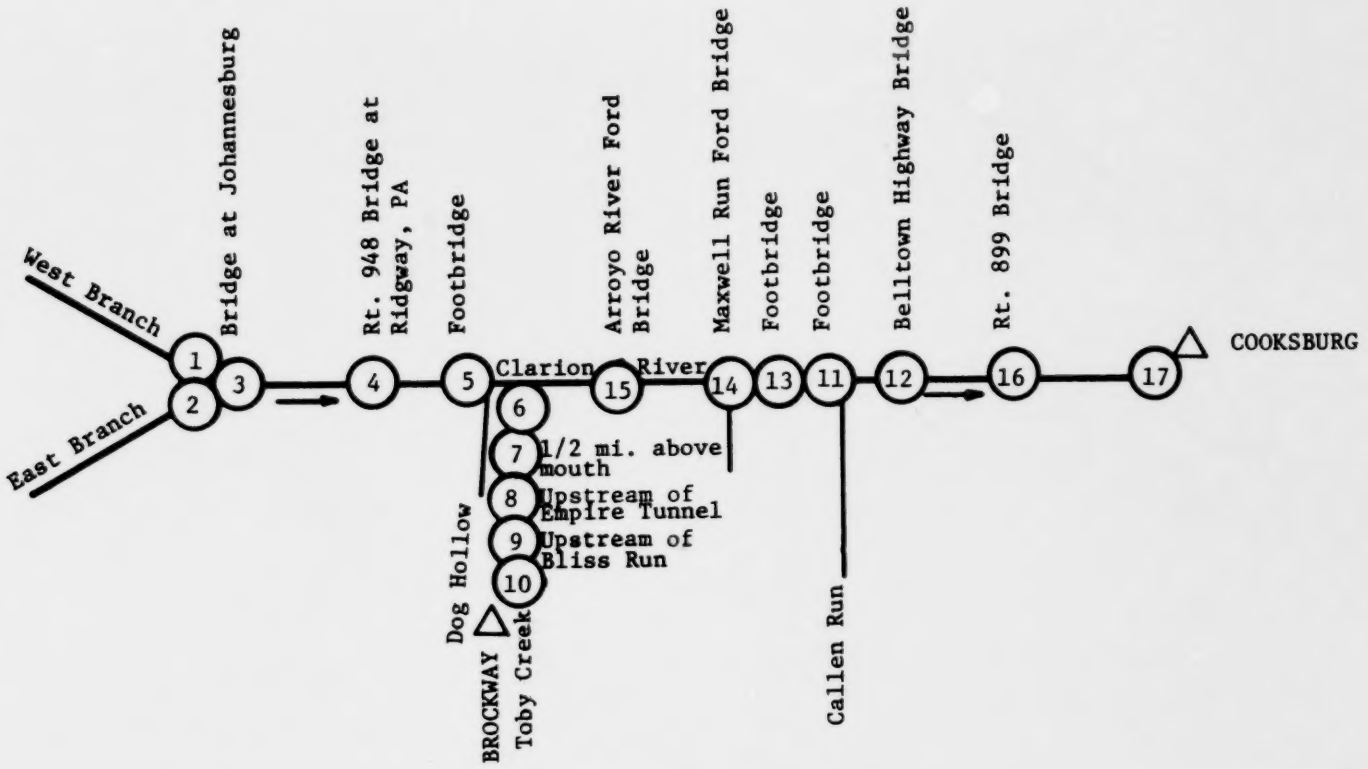


Figure 1. Sampling scheme for the Toby Creek - Clarion River system.

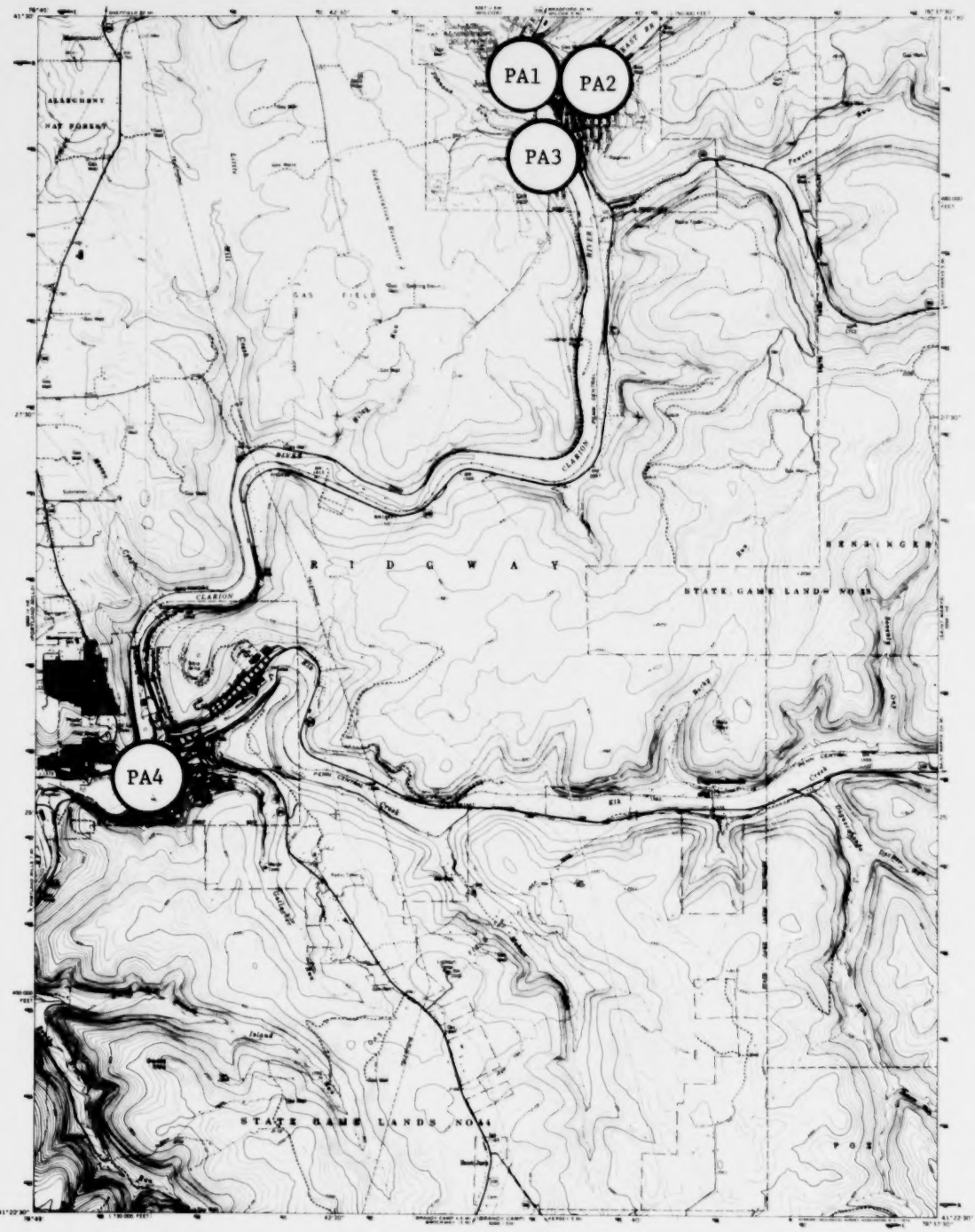


Figure 2. Sampling locations from Ridgway Quadrangle, Pennsylvania.

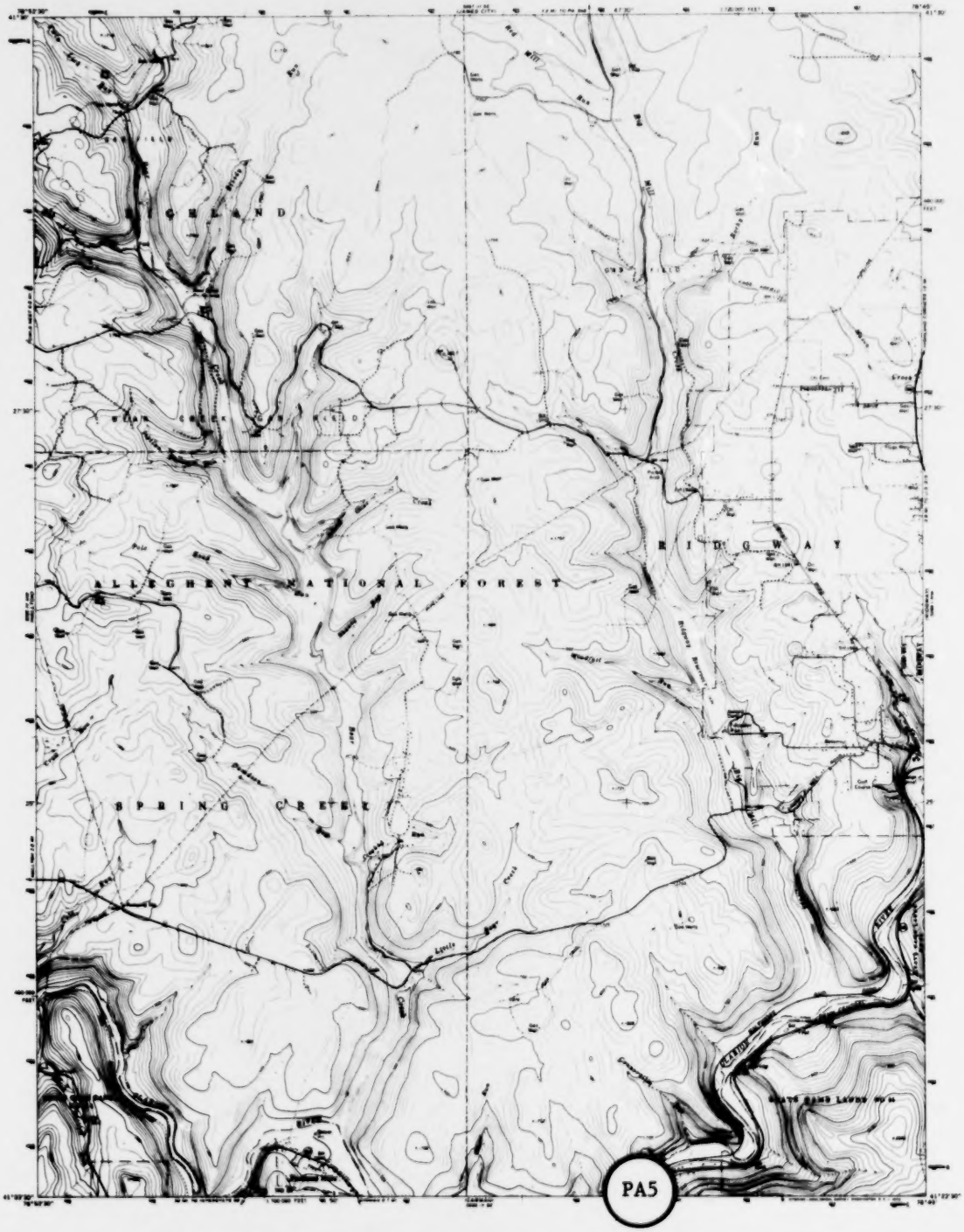


Figure 3. Sampling locations from Portland Mills Quadrangle, Pennsylvania.

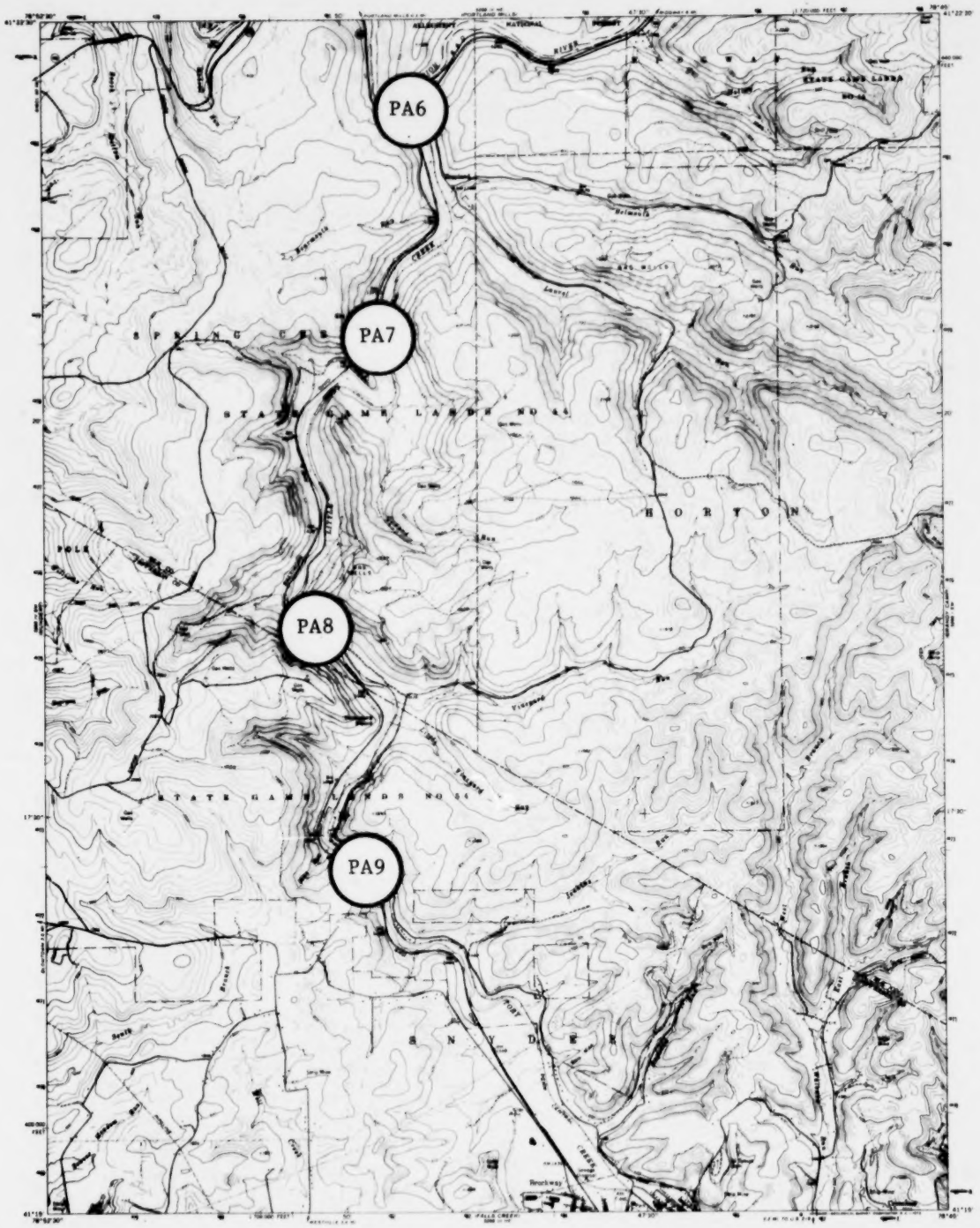


Figure 4. Sampling locations from Carman Quadrangle, Pennsylvania.

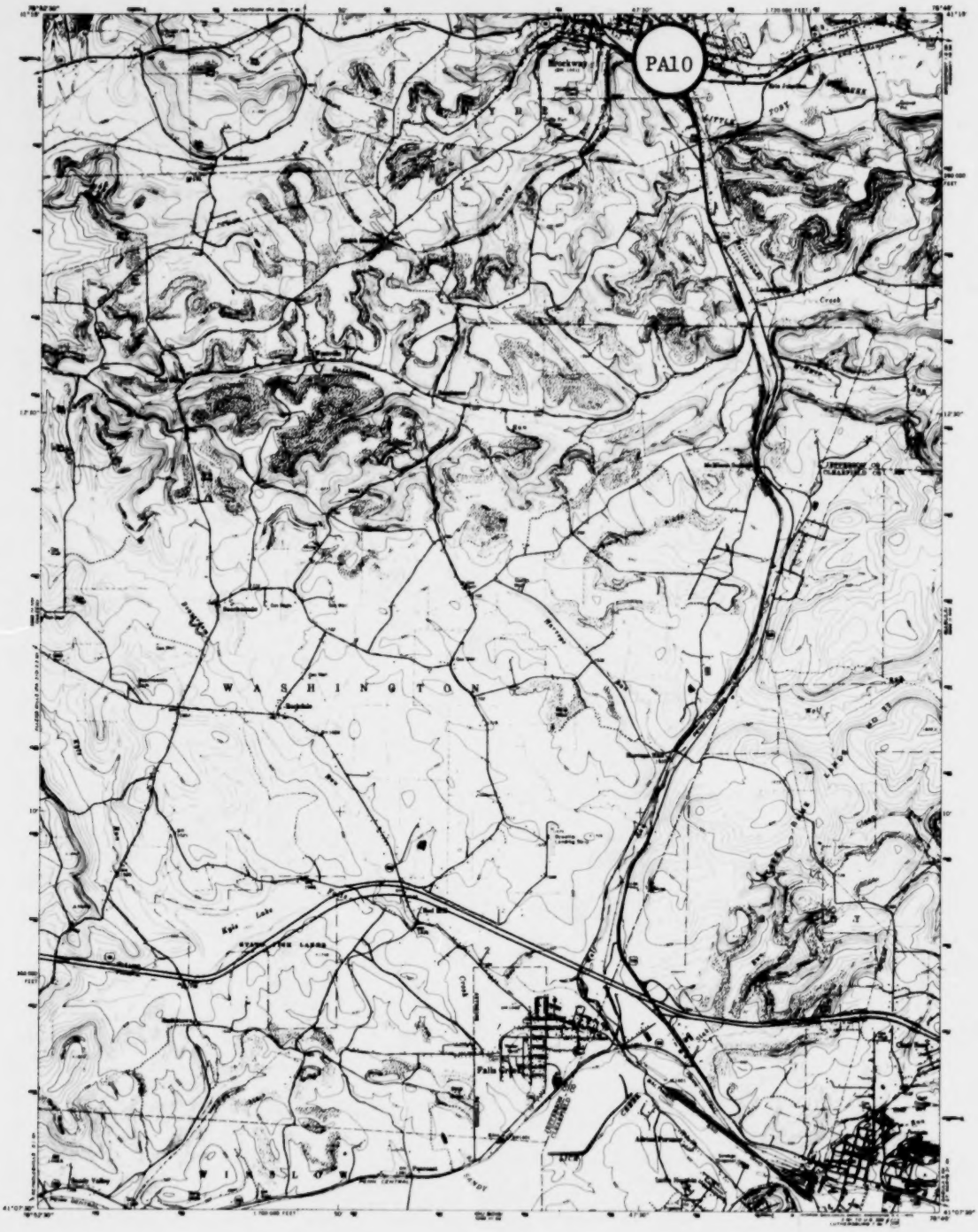


Figure 5. Sampling location from Falls Creek Quadrangle, Pennsylvania.

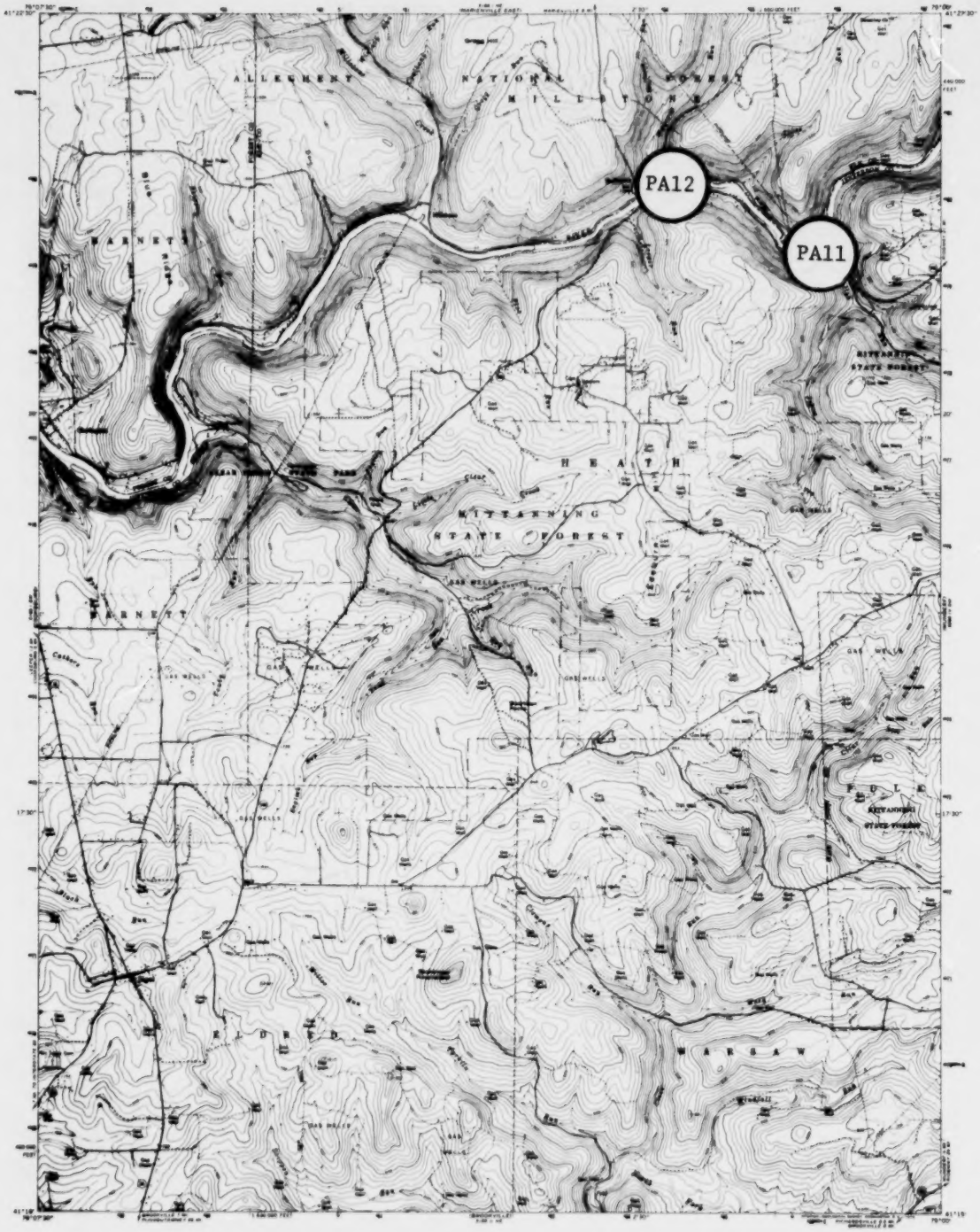


Figure 6. Sampling locations from Sigel Quadrangle, Pennsylvania.

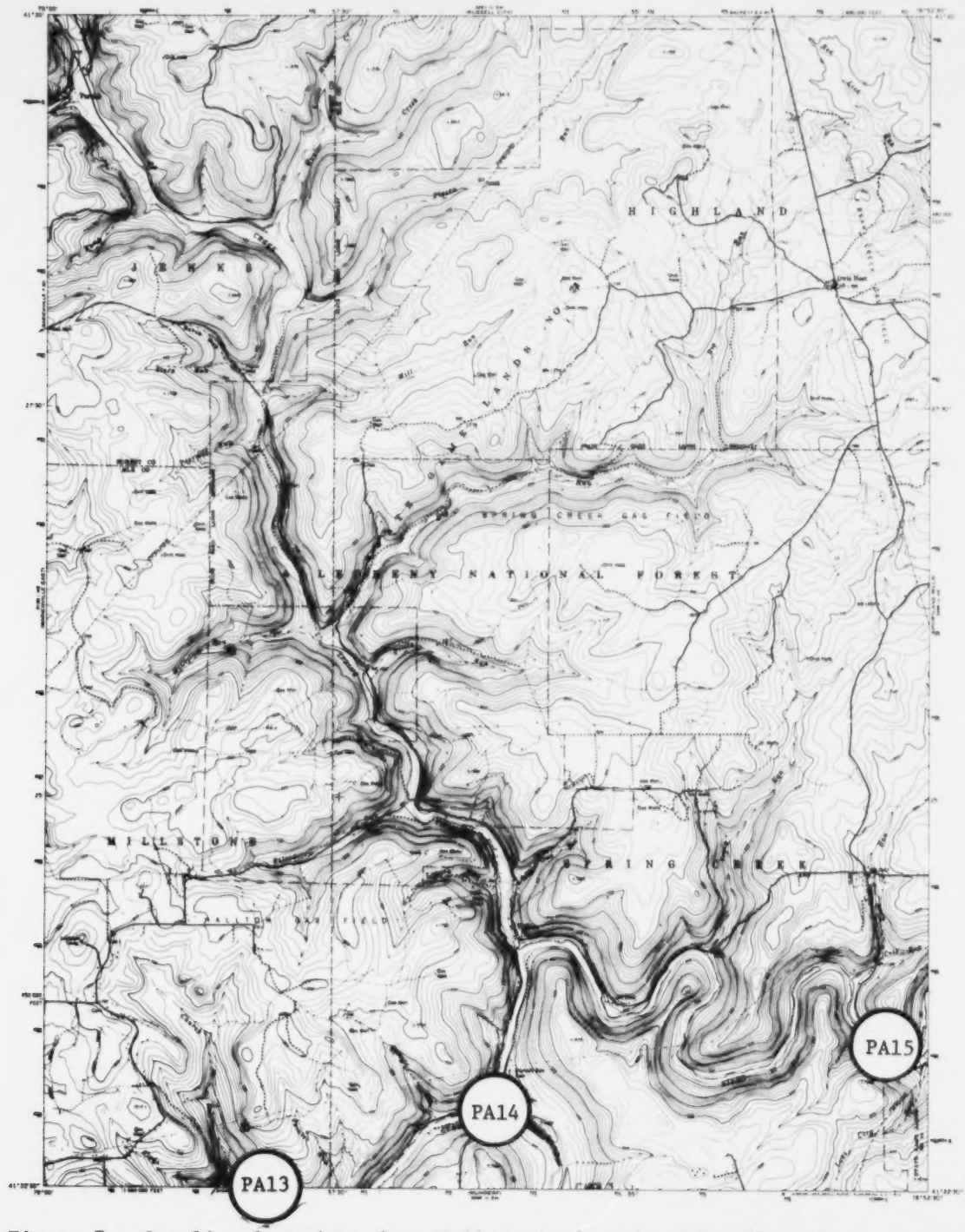


Figure 7. Sampling locations from Hallton Quadrangle, Pennsylvania.

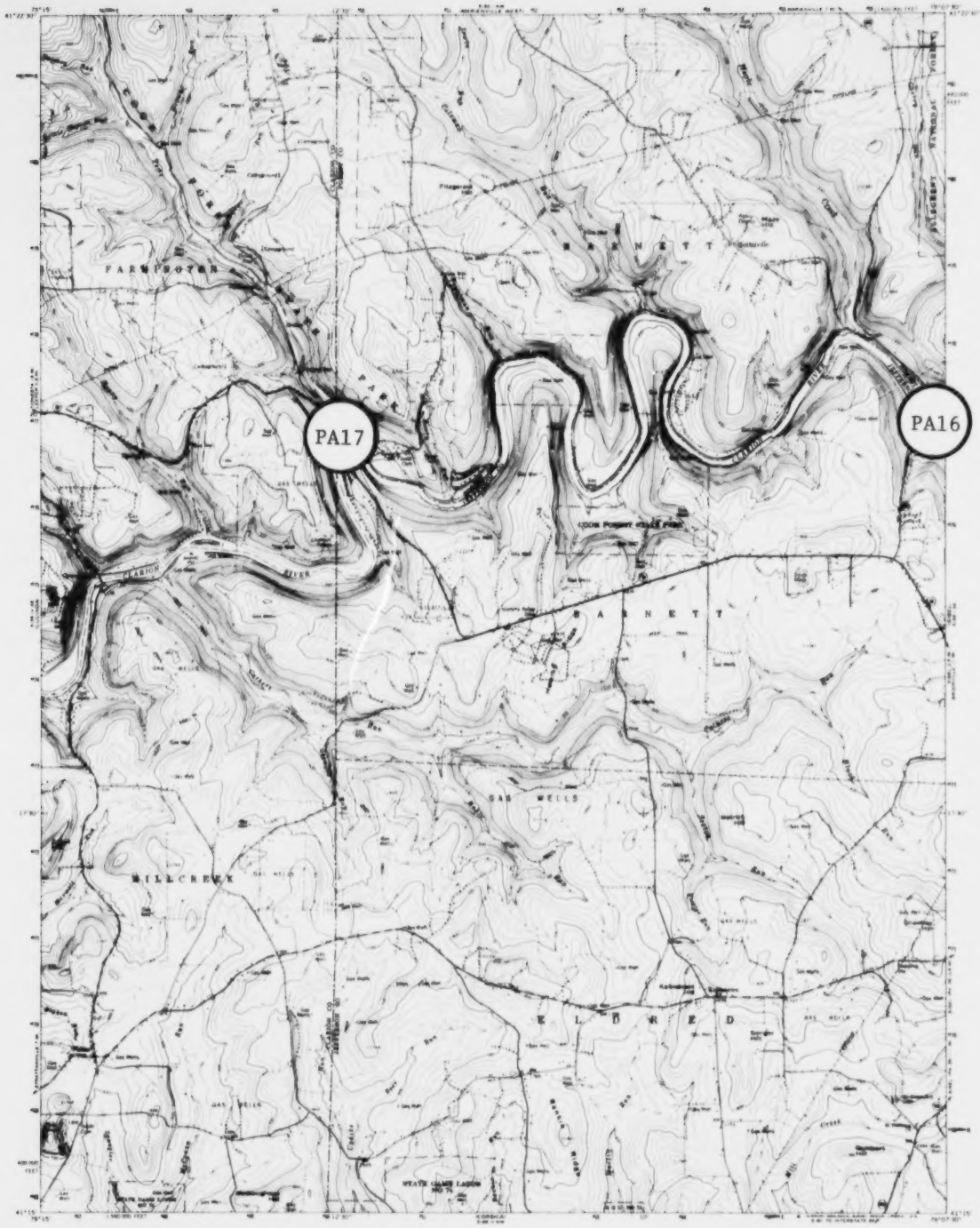


Figure 8. Sampling locations from Cooksburg Quadrangle, Pennsylvania.

Figure 9. Aerial photograph of Gulfport, Mississippi, area in the vicinity of Plant Jack Watson.

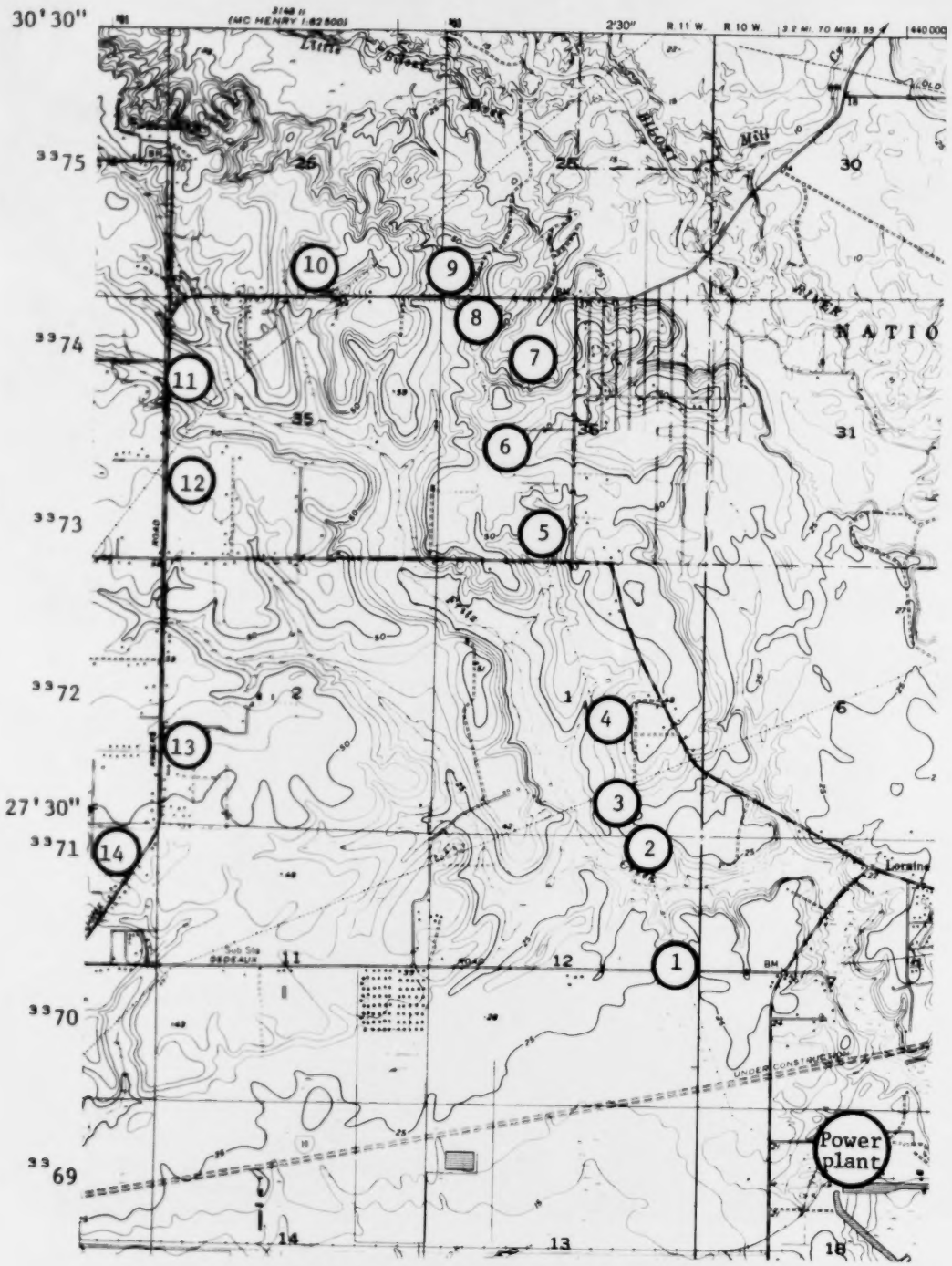


Figure 10. Sampling locations from Gulfport North Quadrangle, Mississippi.

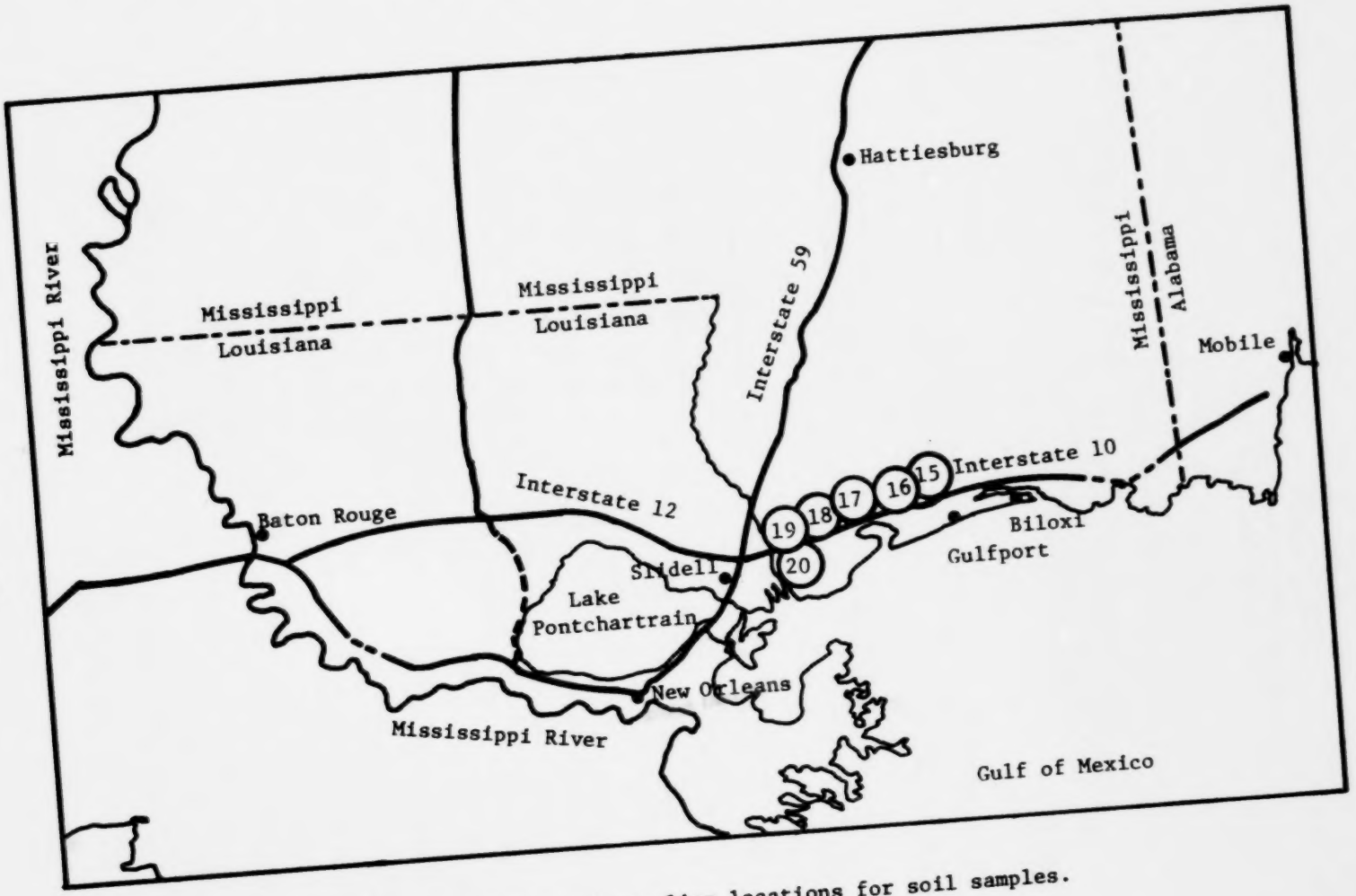


Figure 11. Background sampling locations for soil samples.

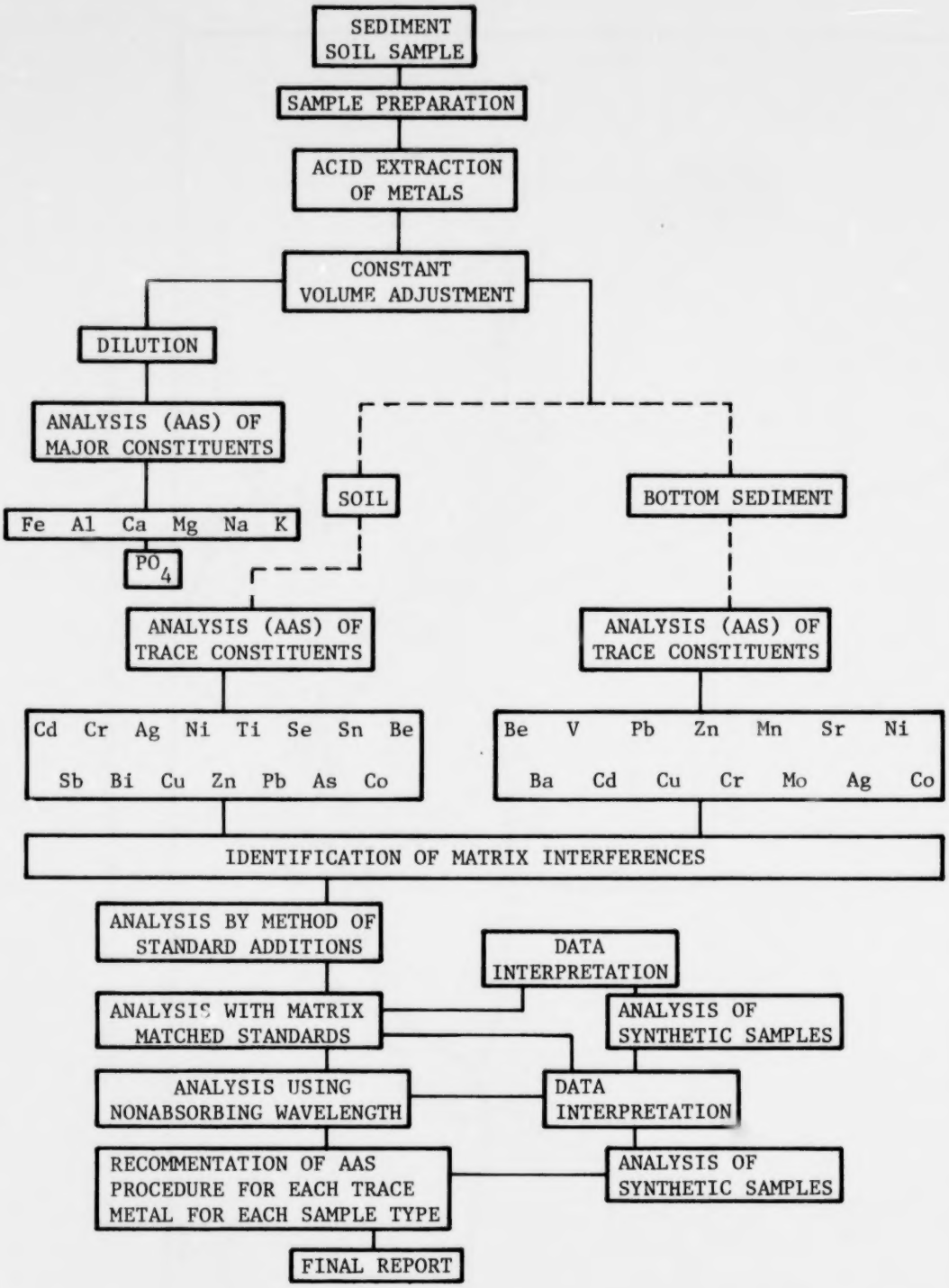

SEDIMENT SOIL SAMPLE
SAMPLE PREPARATION
ACID EXTRACTION OF METALS
CONSTANT VOLUME ADJUSTMENT
DILUTION
ANALYSIS (AAS) OF MAJOR CONSTITUENTS
Fe Al Ca Mg Na K
PO_4
SOIL
BOTTOM SEDIMENT
ANALYSIS (AAS) OF TRACE CONSTITUENTS
ANALYSIS (AAS) OF TRACE CONSTITUENTS
Cd Cr Ag Ni Ti Se Sn Be Sb Bi Cu Zn Pb As Co
Be V Pb Zn Mn Sr Ni Ba Cd Cu Cr Mo Ag Co
IDENTIFICATION OF MATRIX INTERFERENCES
ANALYSIS BY METHOD OF STANDARD ADDITIONS
DATA INTERPRETATION
ANALYSIS WITH MATRIX MATCHED STANDARDS
ANALYSIS OF SYNTHETIC SAMPLES
ANALYSIS USING NONABSORBING WAVELENGTH
DATA INTERPRETATION
RECOMMENTATION OF AAS PROCEDURE FOR EACH TRACE METAL FOR EACH SAMPLE TYPE
ANALYSIS OF SYNTHETIC SAMPLES
FINAL REPORT

Figure 12. Schematic of experimental approach.

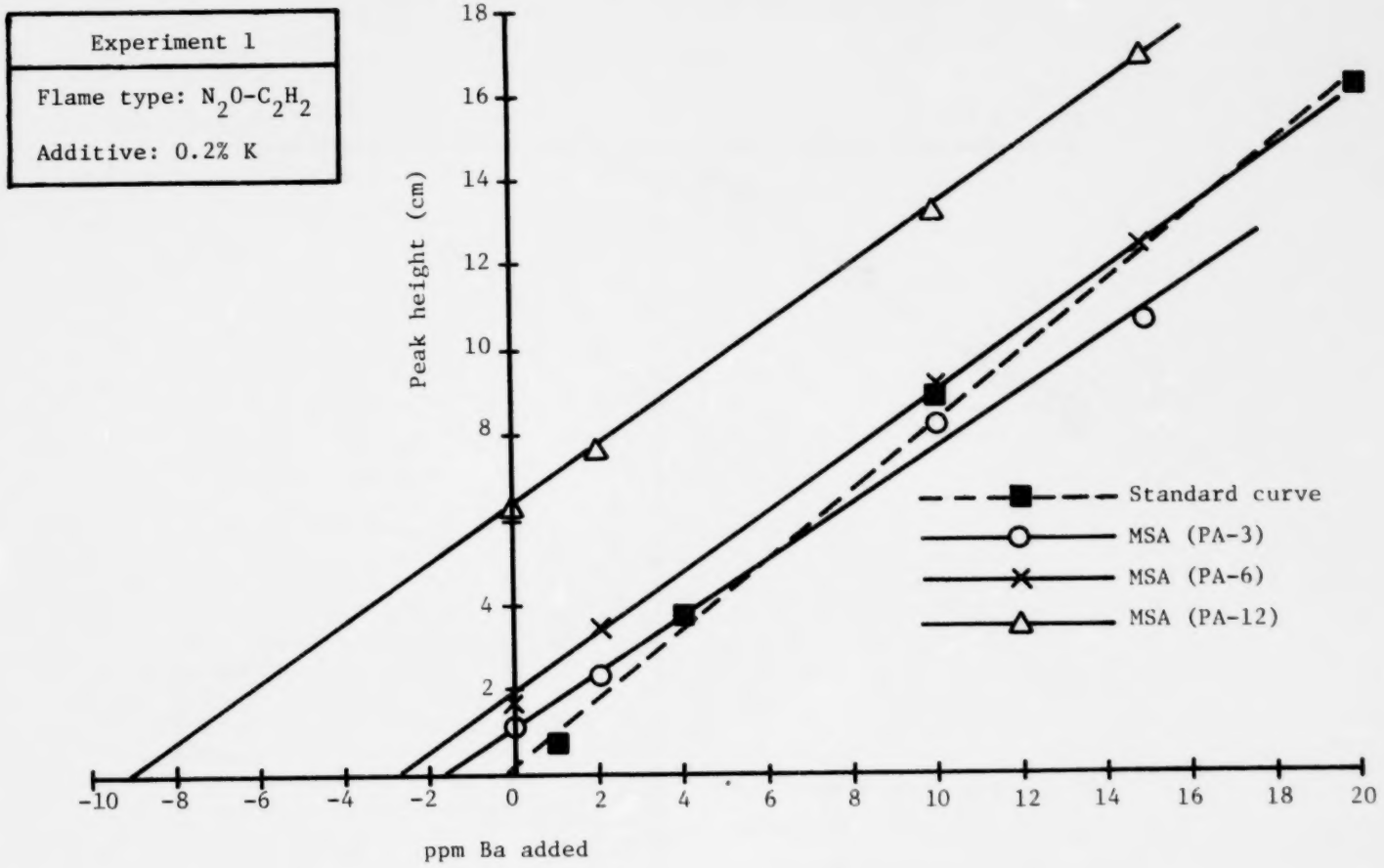


Figure 13. MSA plot for barium - Experiment 1.

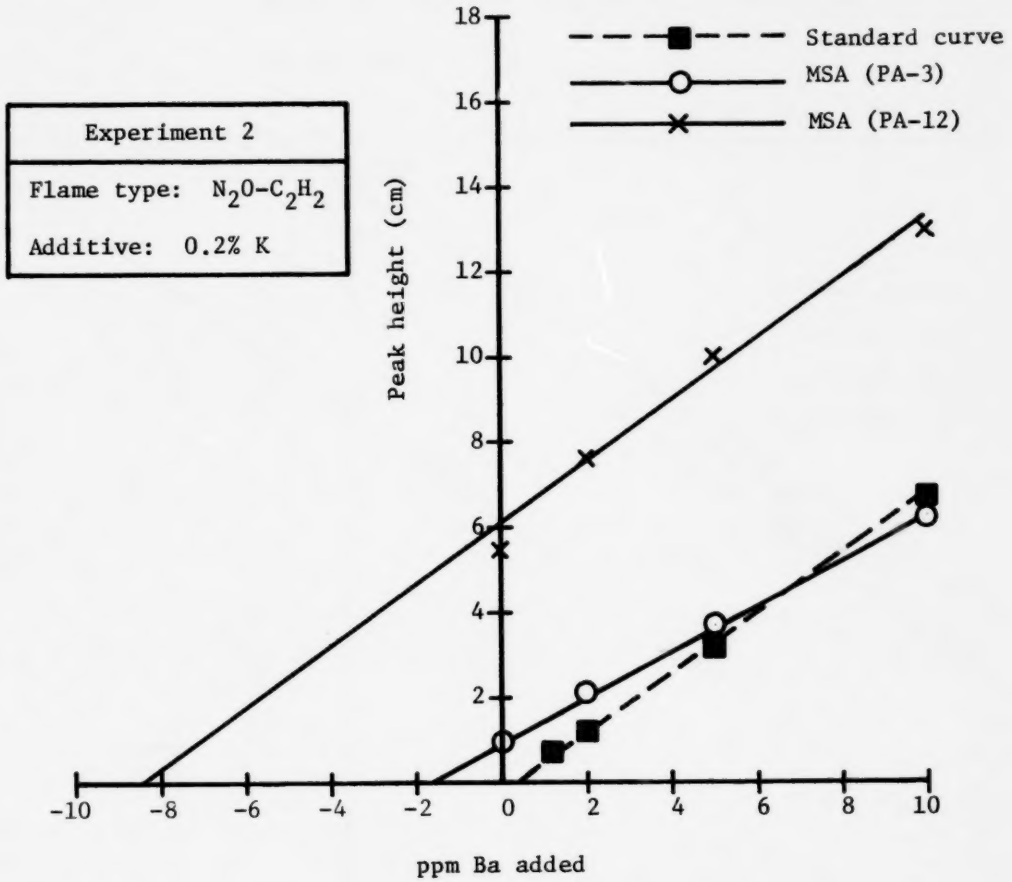


Figure 14. MSA plot for barium - Experiment 2.

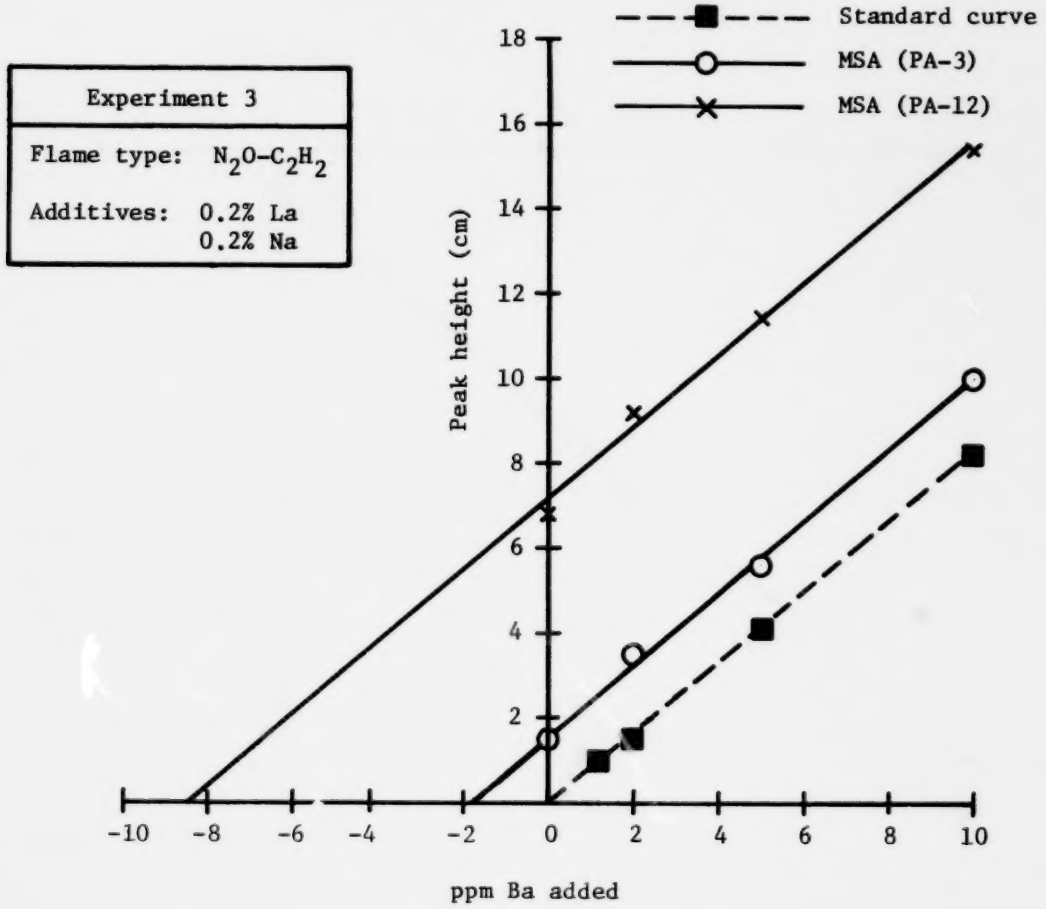


Figure 15. MSA plot for barium - Experiment 3.

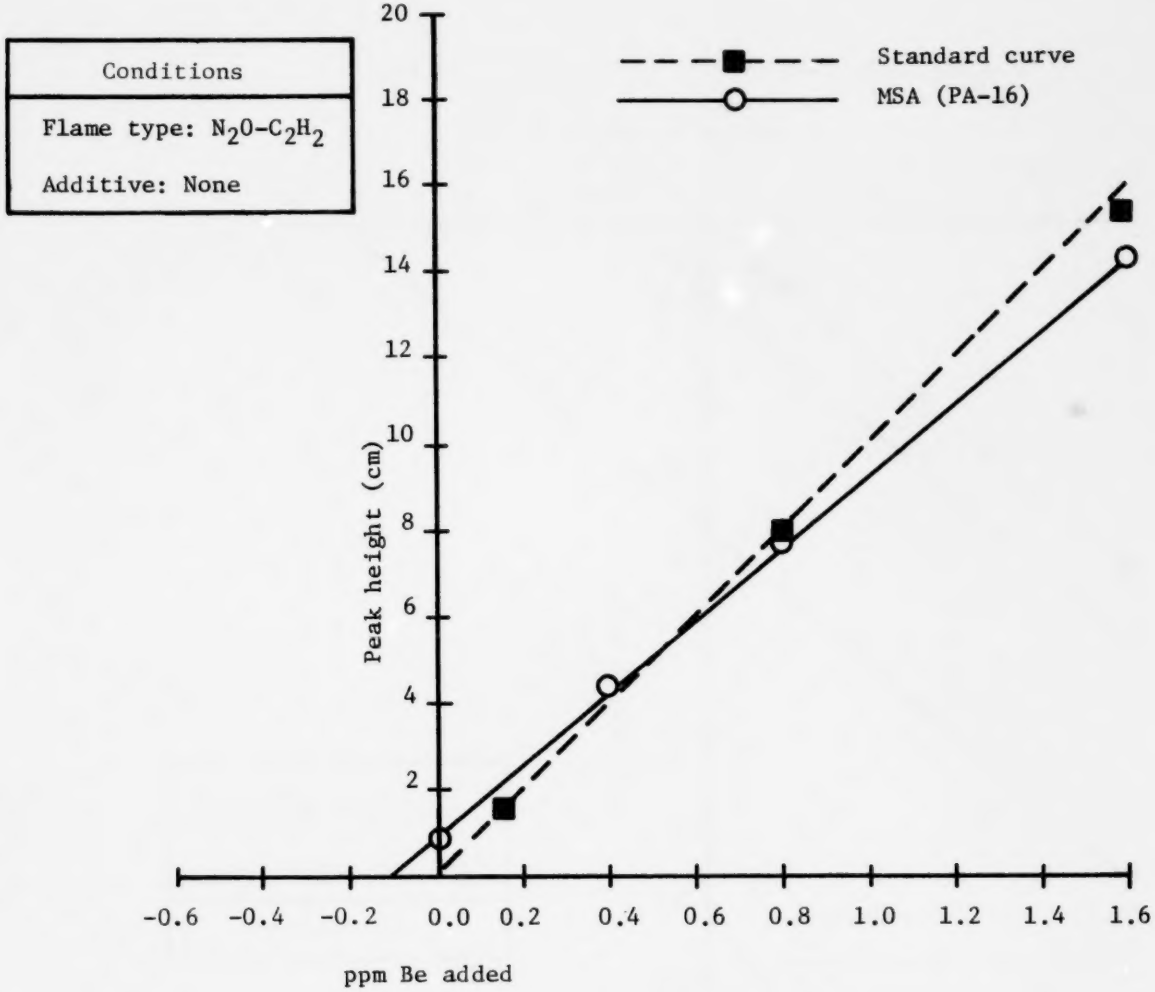


Figure 16. MSA plot for beryllium.

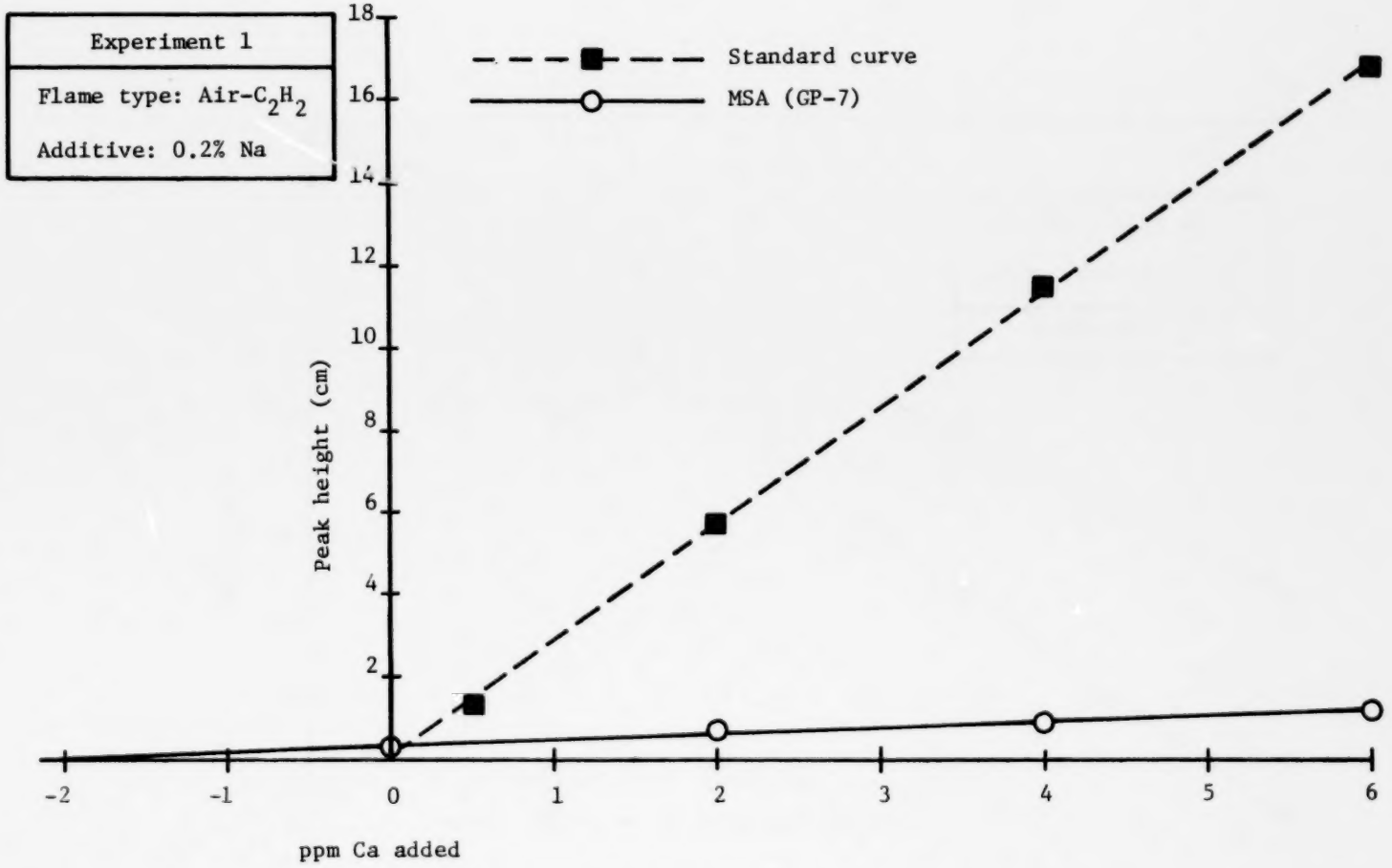


Figure 17. MSA plot for calcium - Experiment 1.

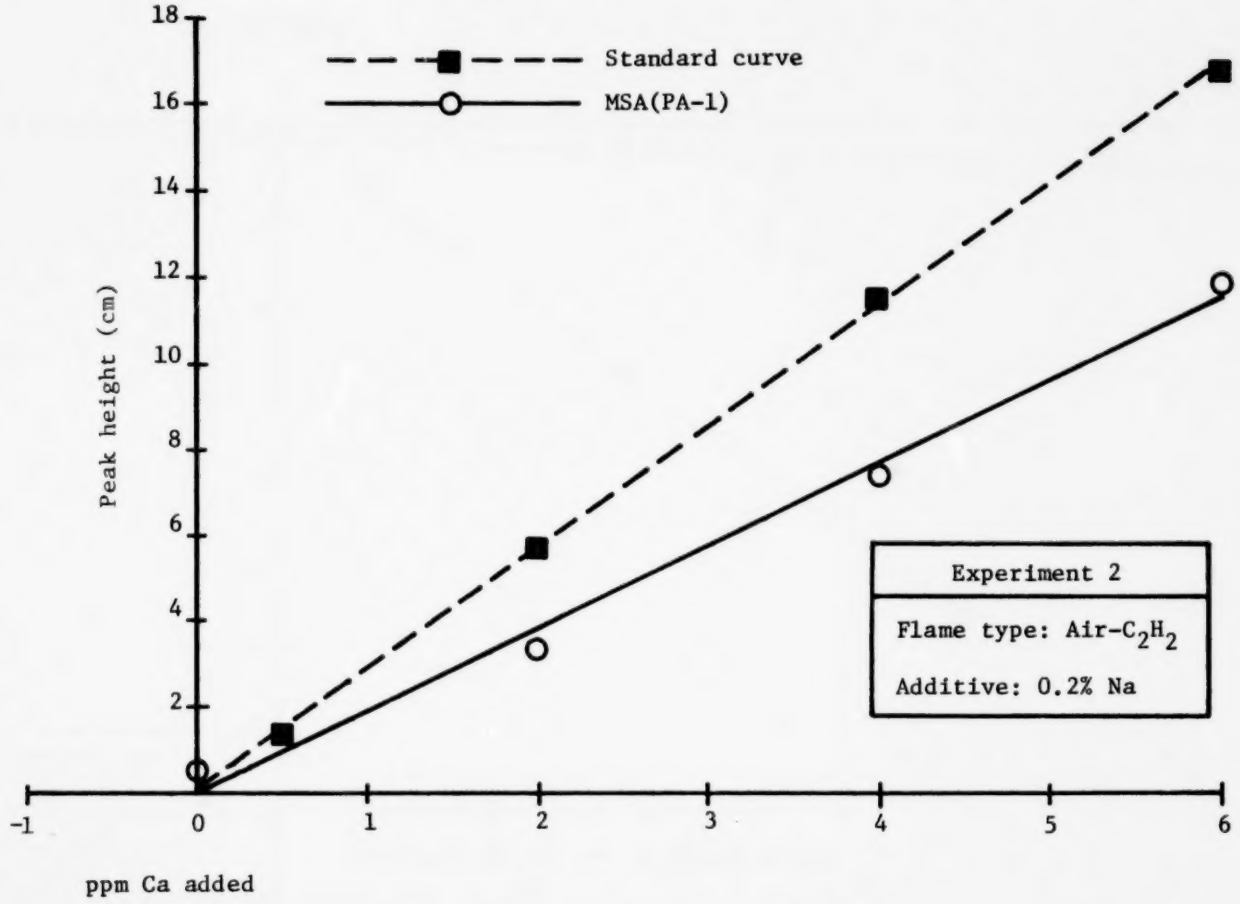


Figure 18. MSA plot for calcium - Experiment 2.

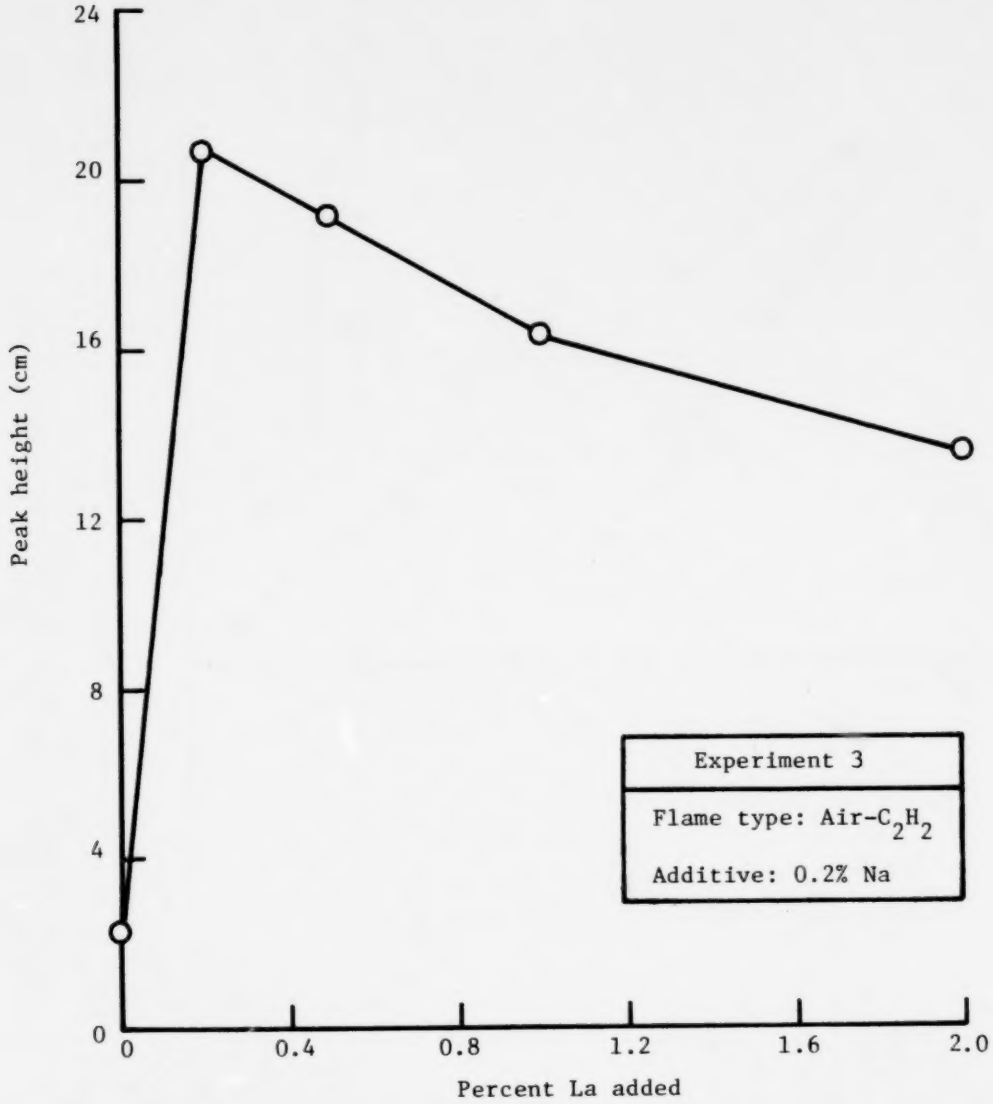


Figure 19. Calcium absorbance of sample PA-1 in the presence of lanthanum - Experiment 3.

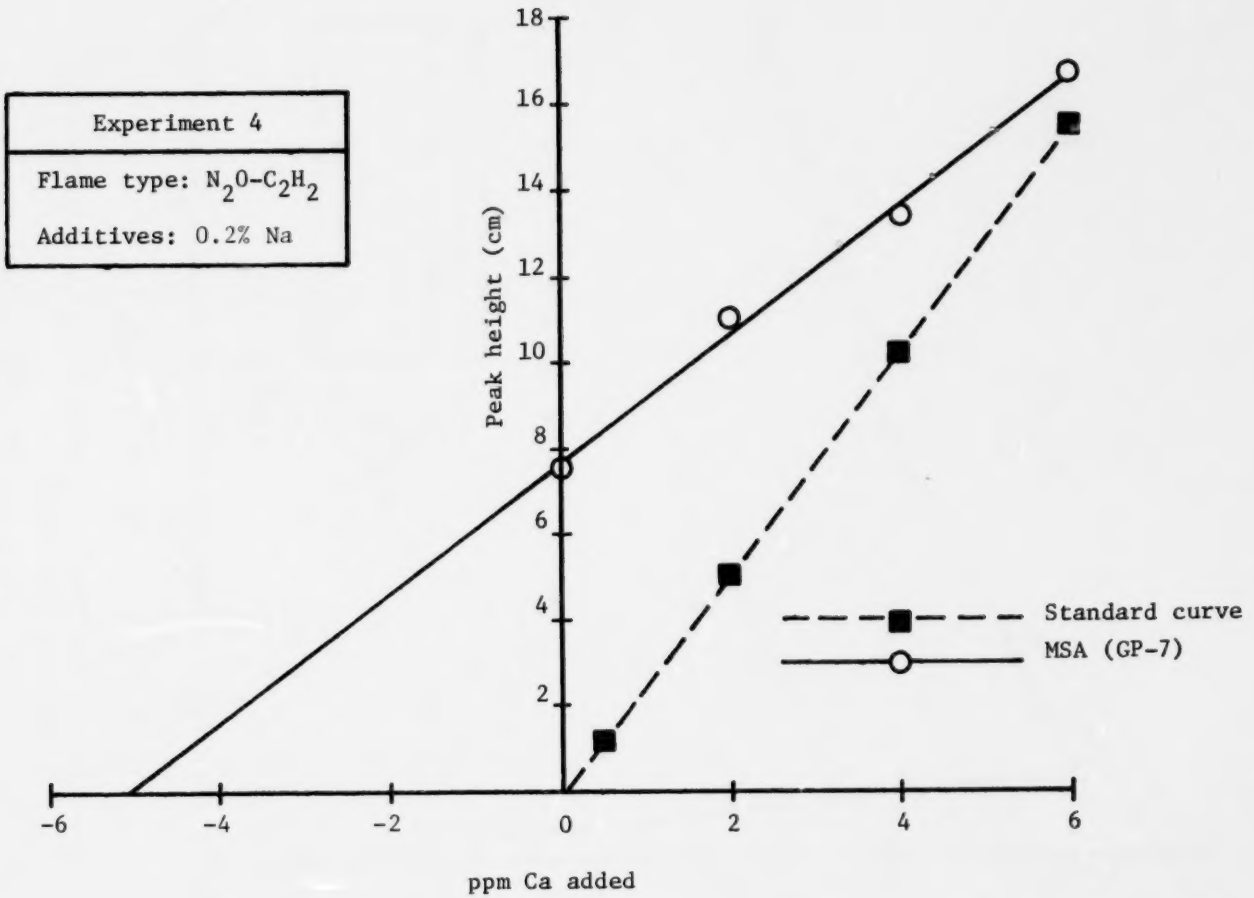


Figure 20. MSA plot for calcium - Experiment 4.

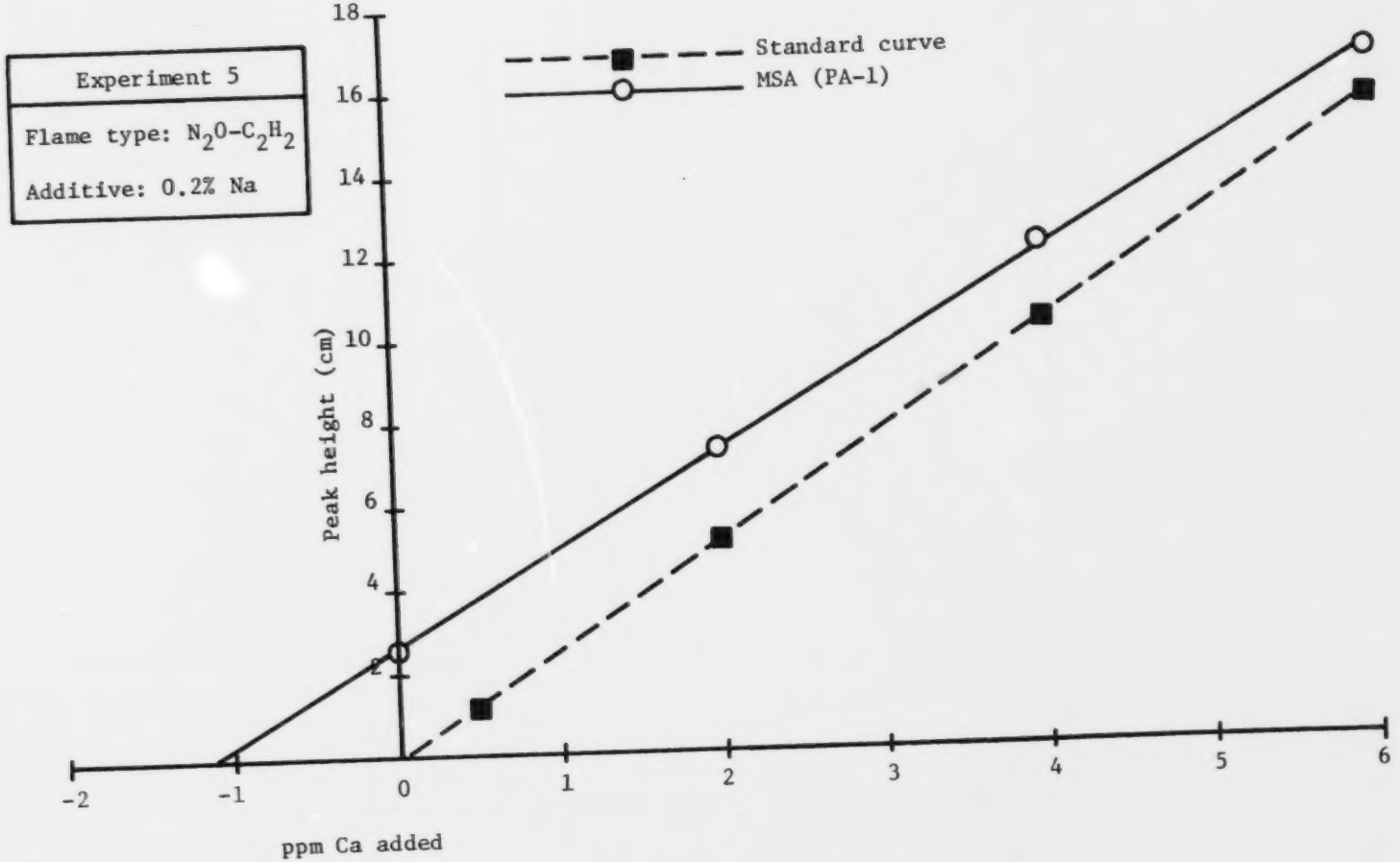


Figure 21. MSA plot for calcium - Experiment 5.

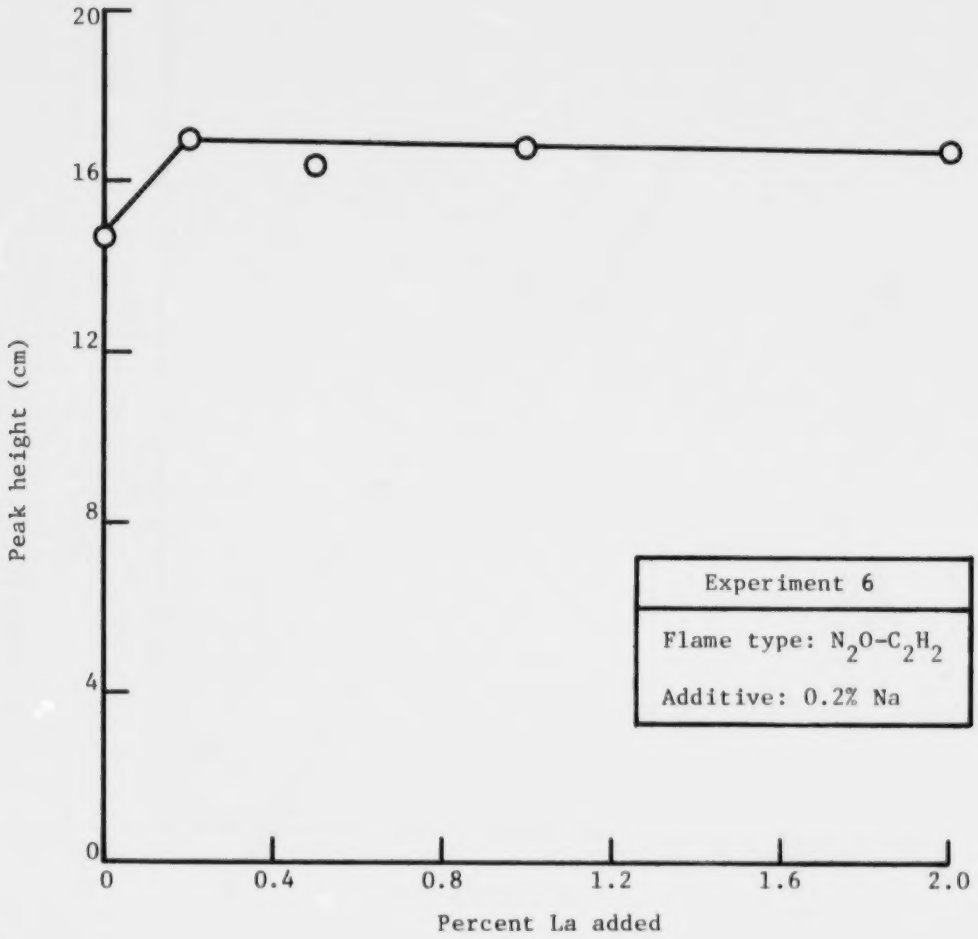


Figure 22. Calcium absorbance of sample PA-1 in the presence of lanthanum - Experiment 6.

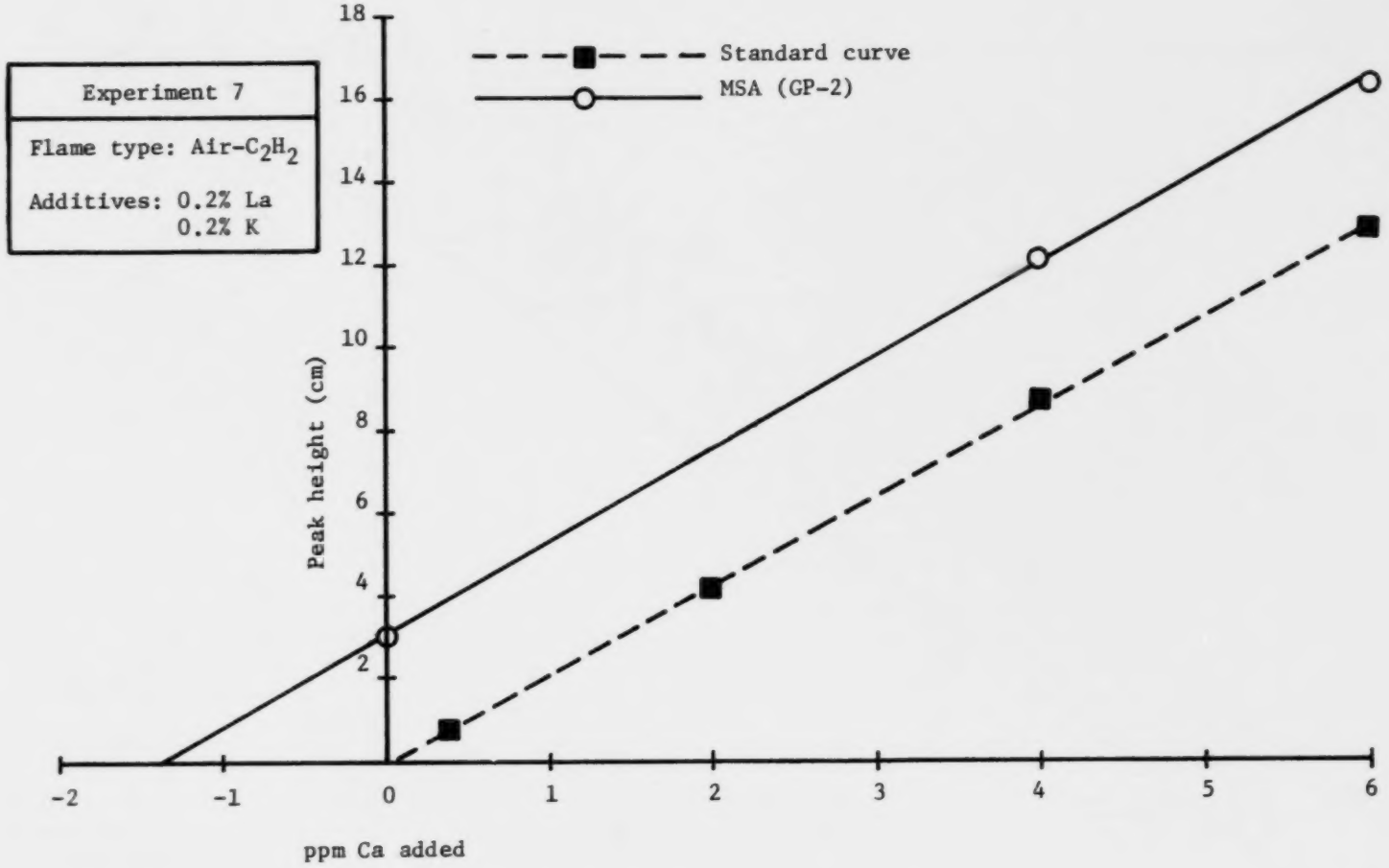


Figure 23. MSA plot for calcium - Experiment 7.

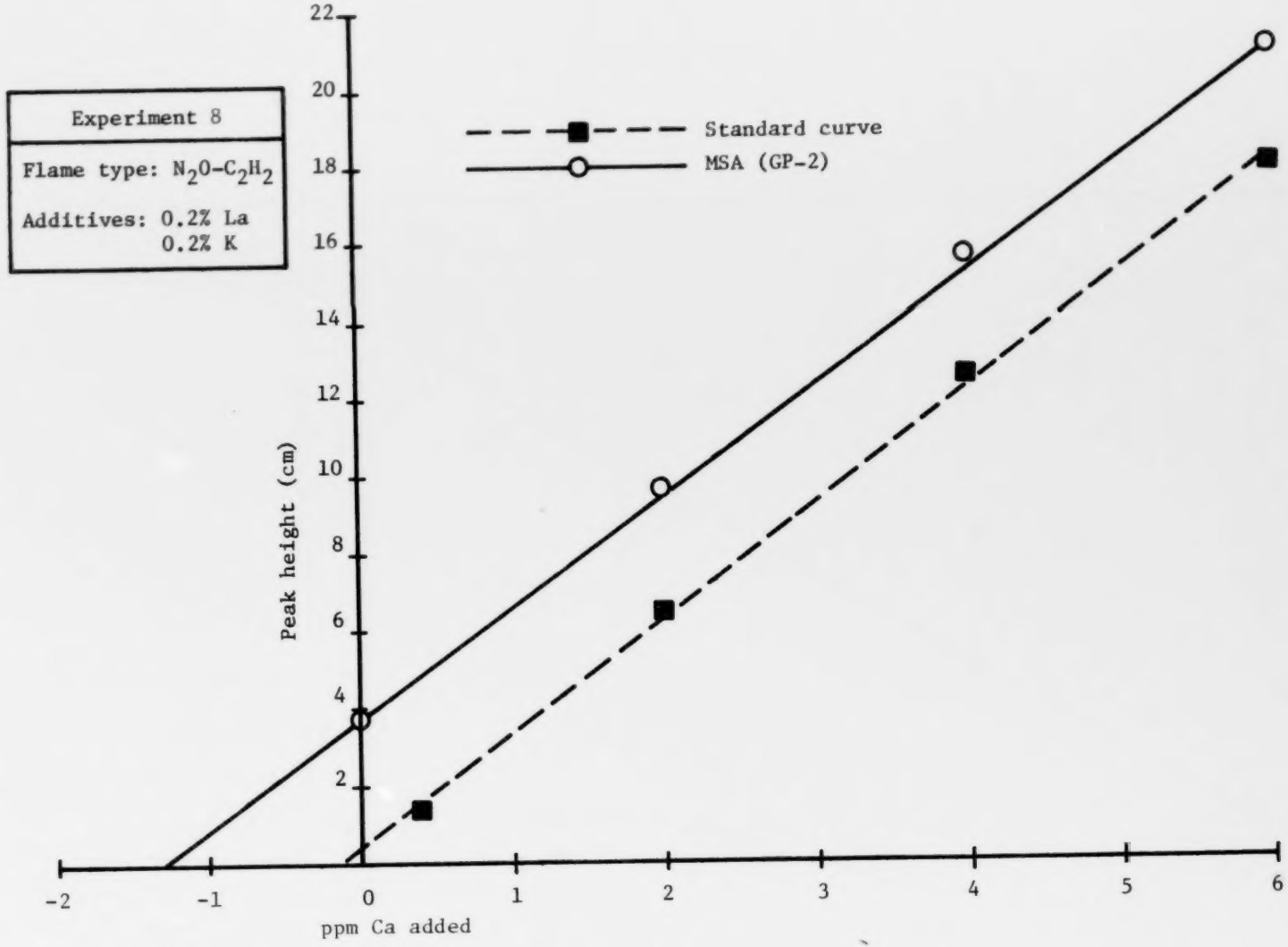


Figure 24. MSA plot for calcium - Experiment 8.

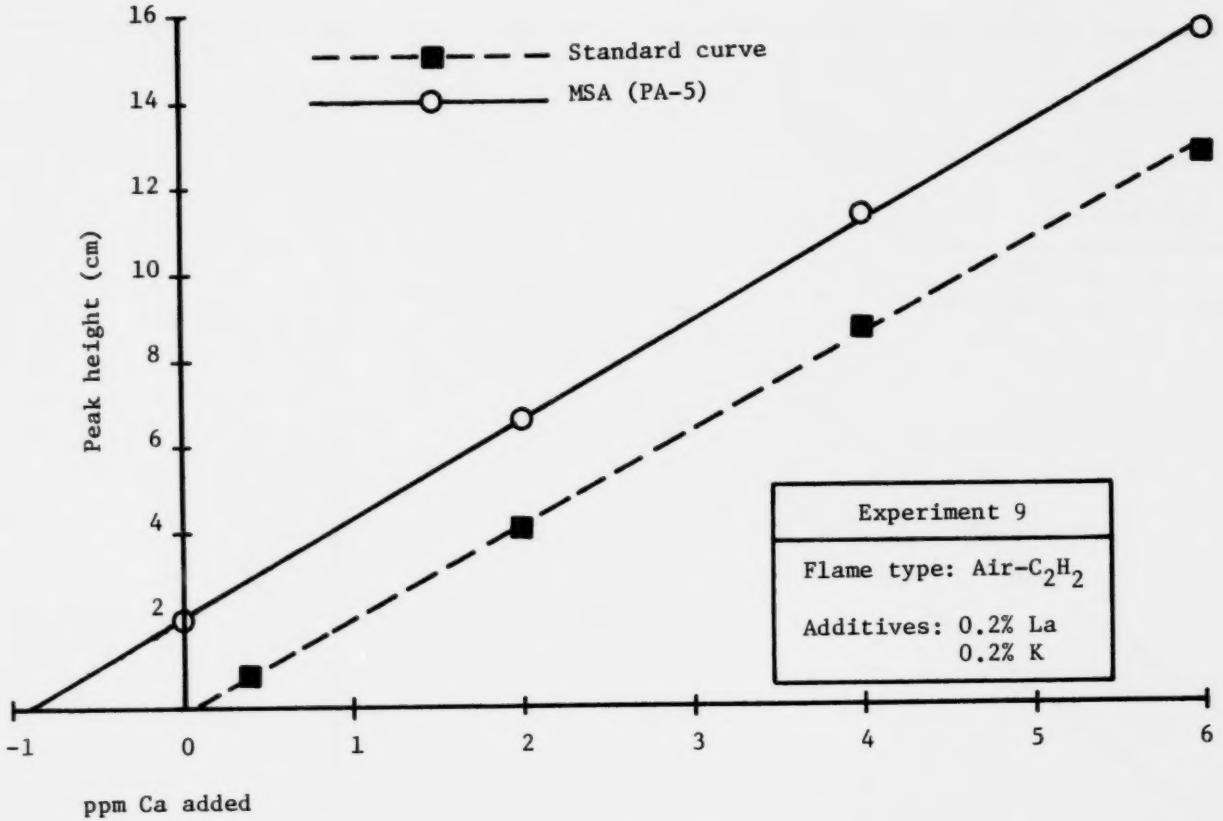


Figure 25. MSA plot for calcium - Experiment 9.

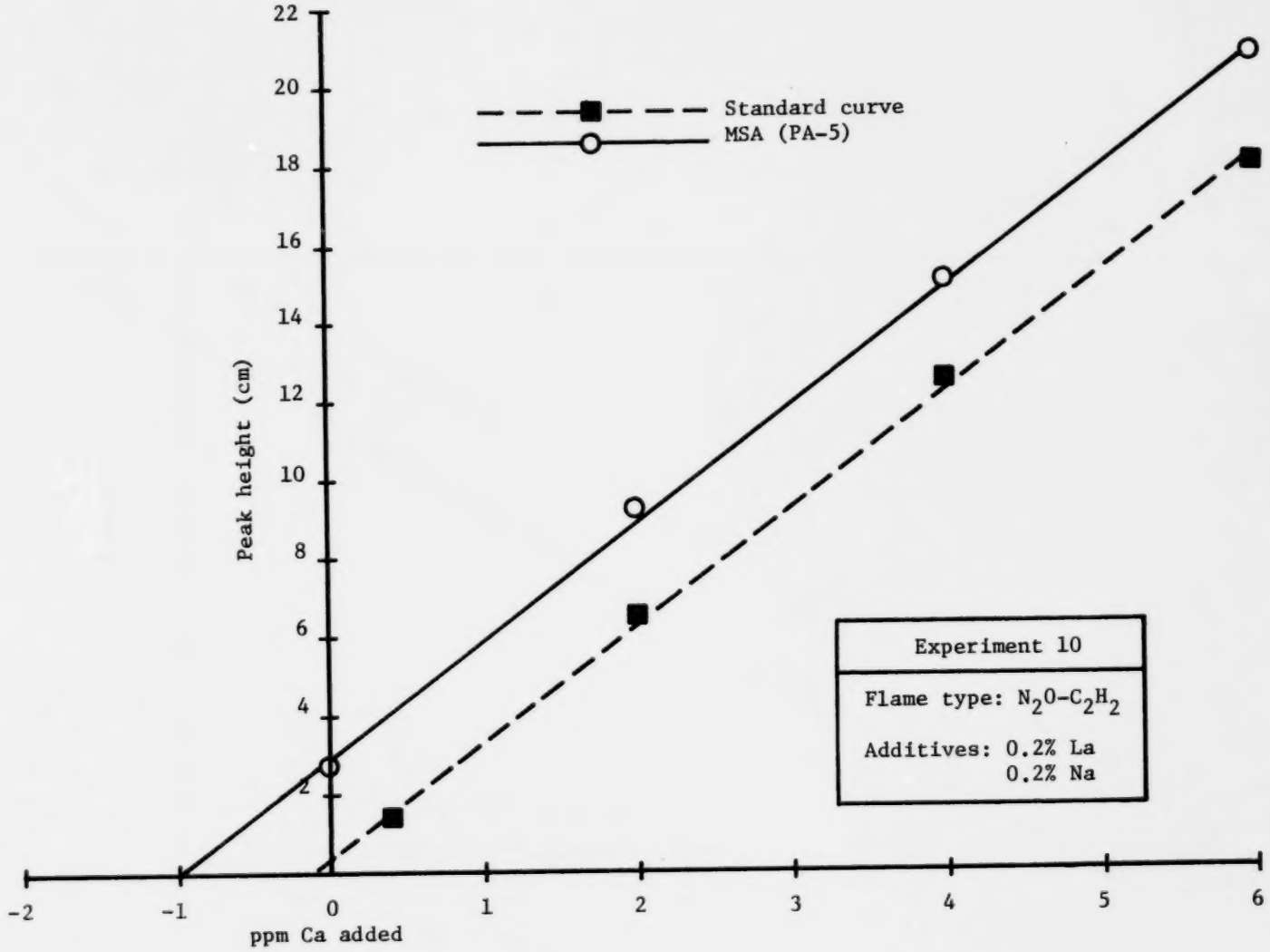


Figure 26. MSA plot for calcium - Experiment 10.

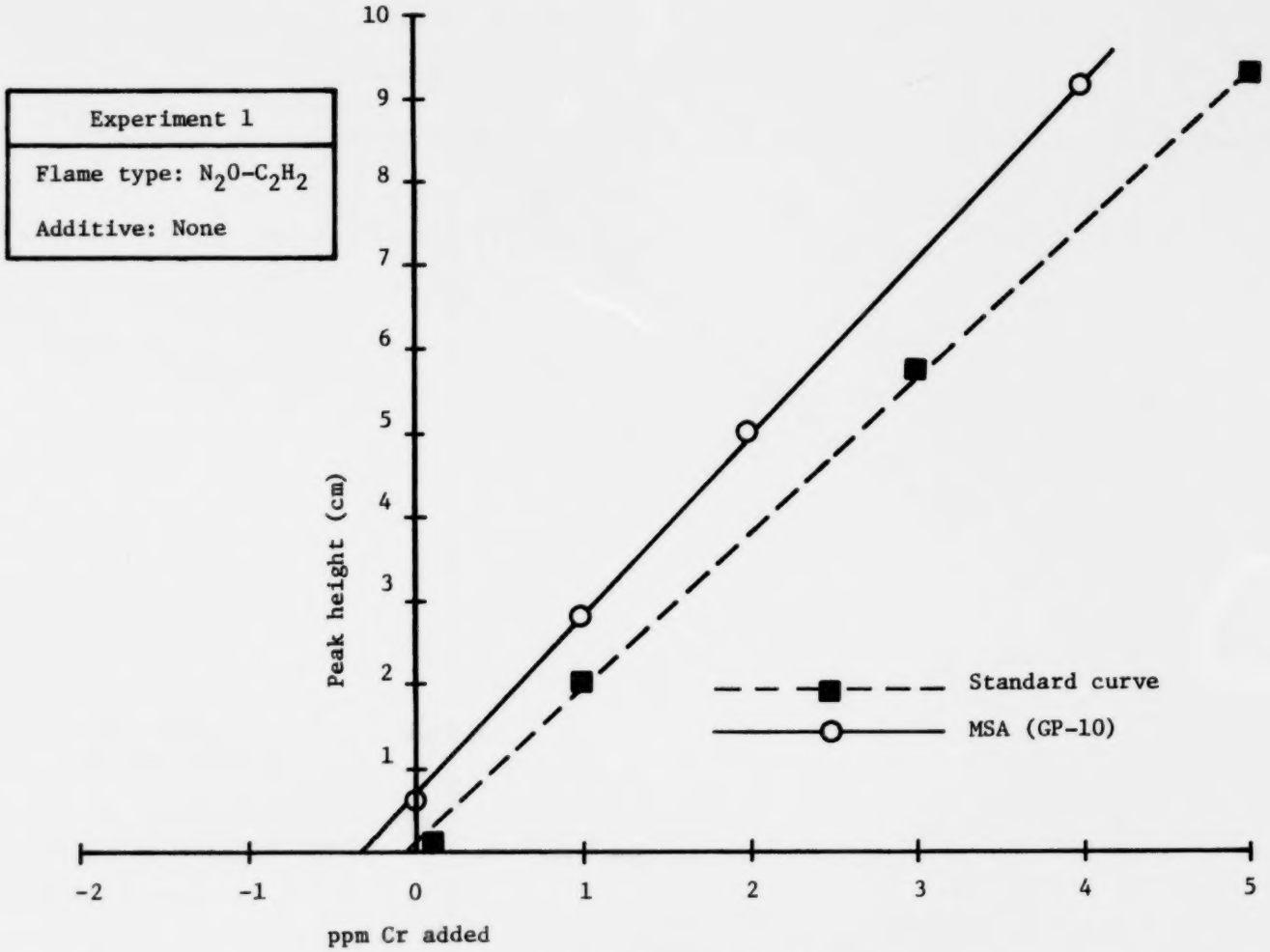


Figure 27. MSA plot for chromium - Experiment 1.

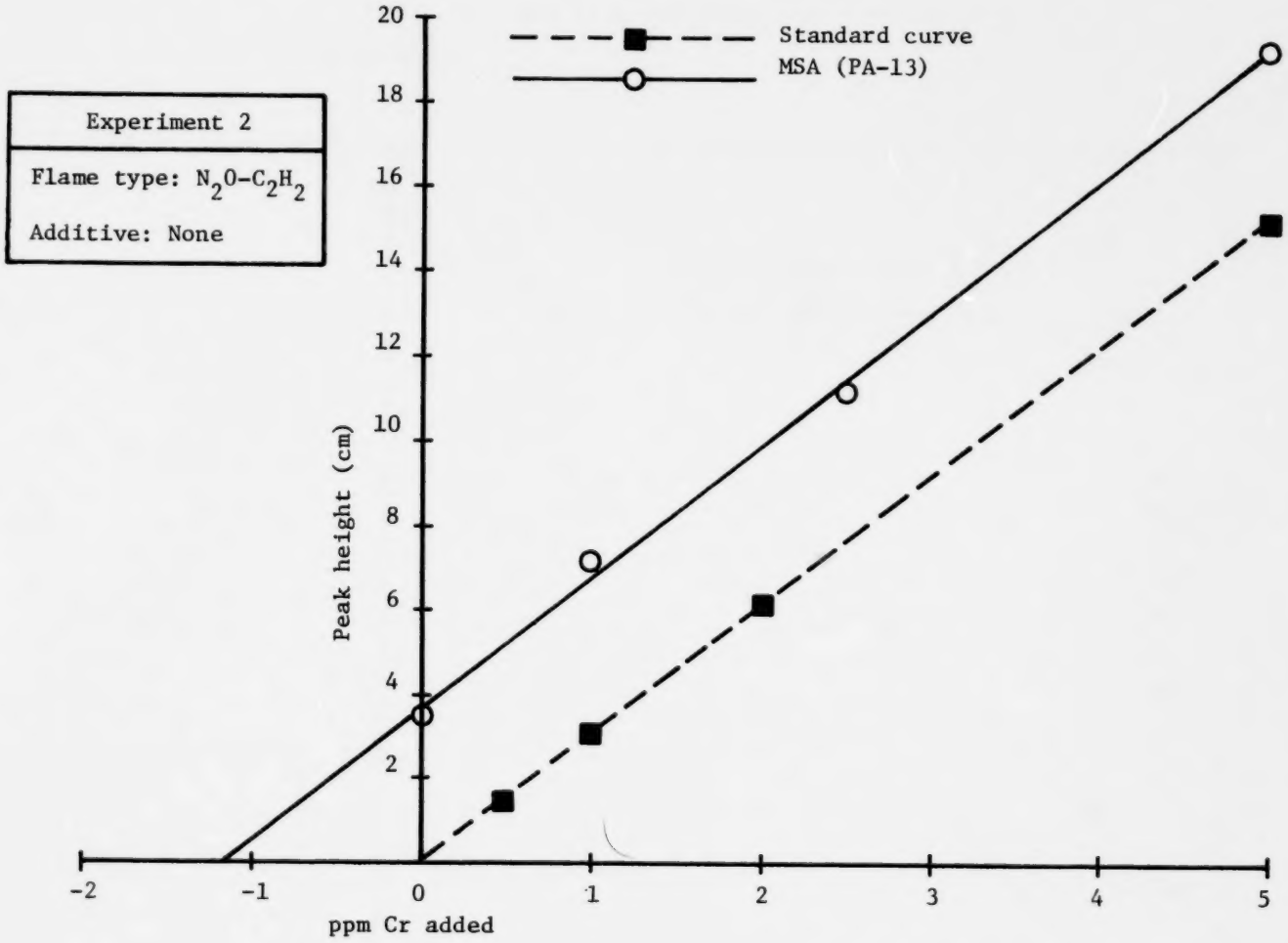


Figure 28. MSA plot for chromium - Experiment 2.

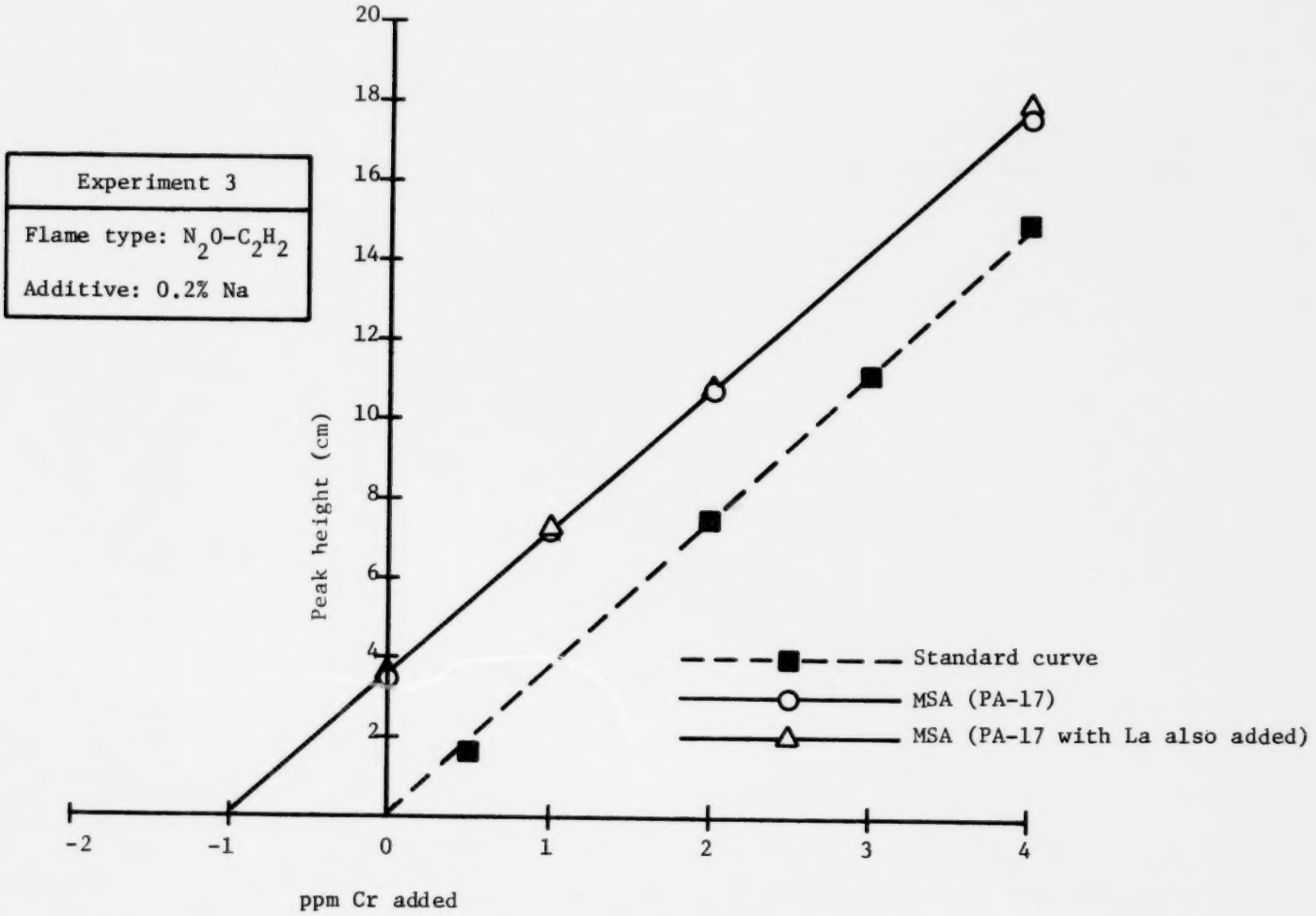


Figure 29. MSA plot for chromium - Experiment 3.

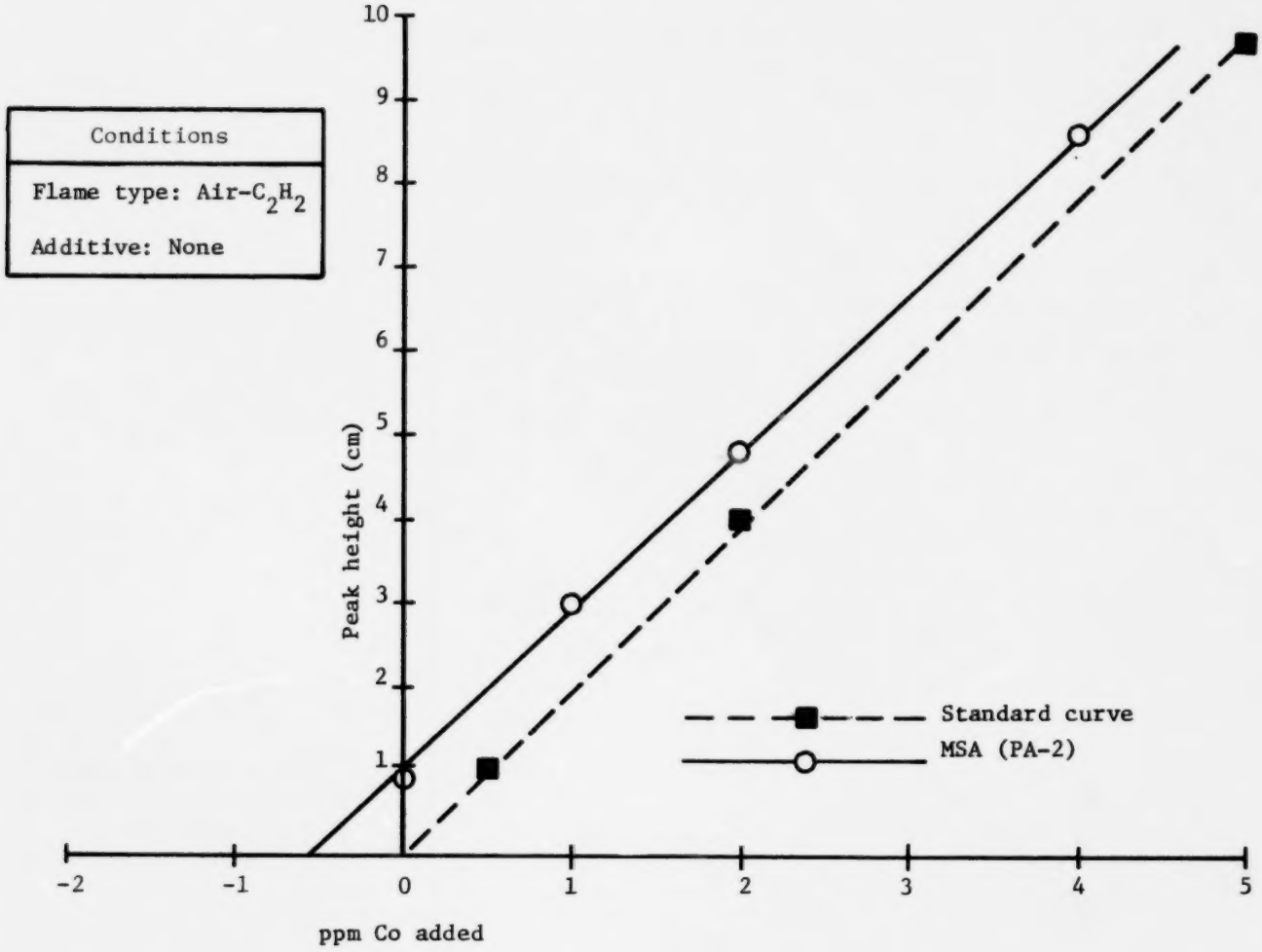


Figure 30. MSA plot for cobalt.

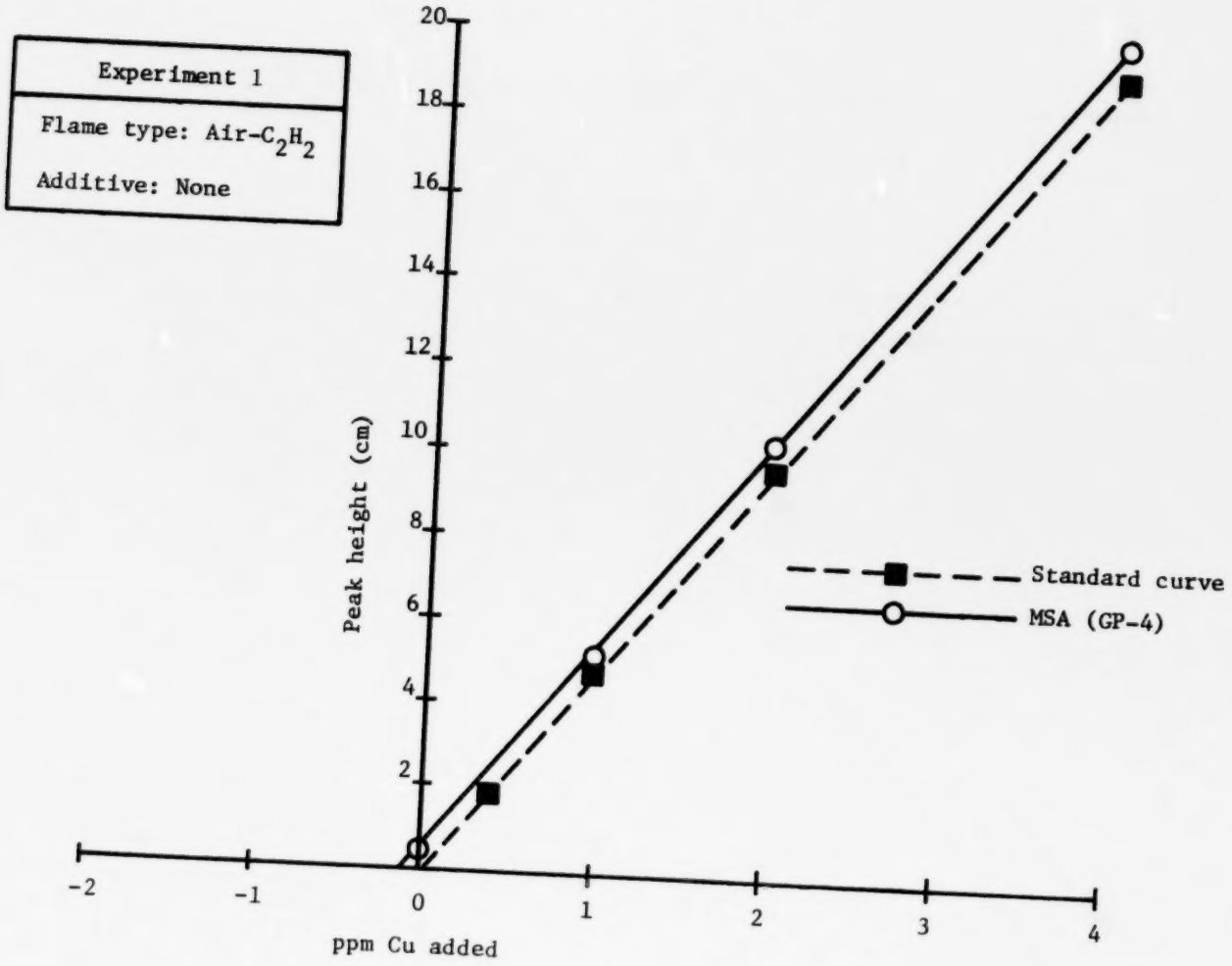


Figure 31. MSA plot for copper - Experiment 1.

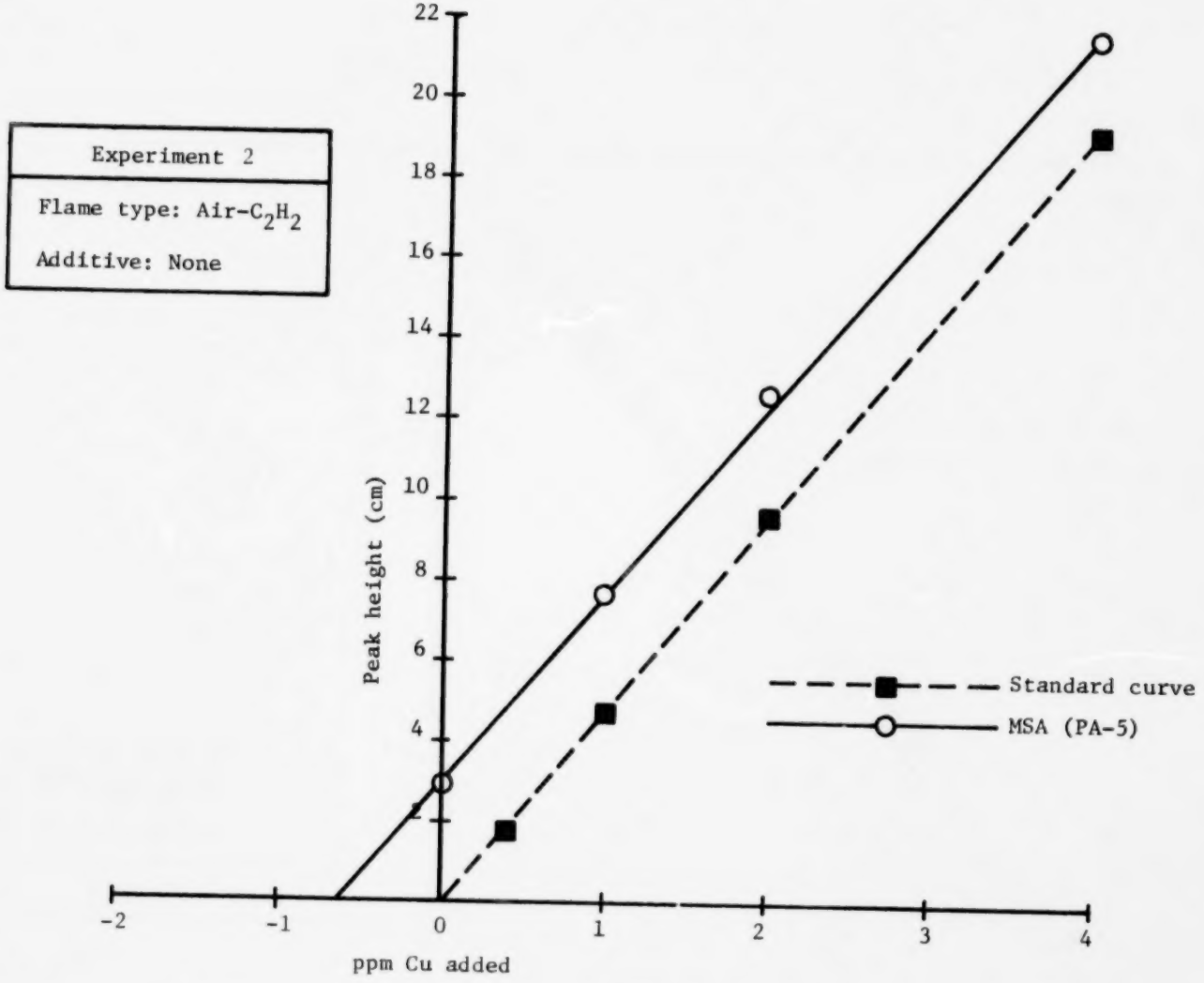


Figure 32. MSA plot for copper - Experiment 2.

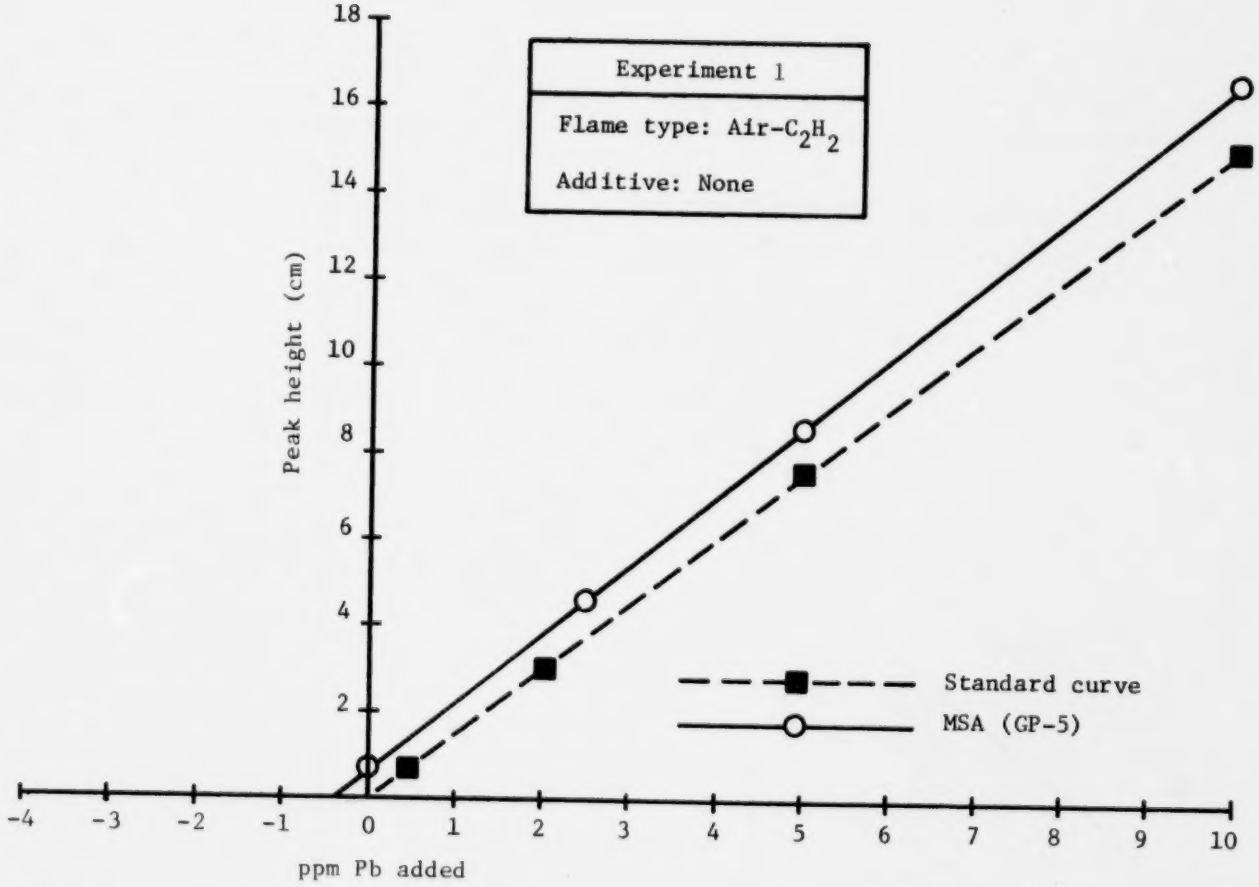


Figure 33. MSA plot for lead - Experiment 1.

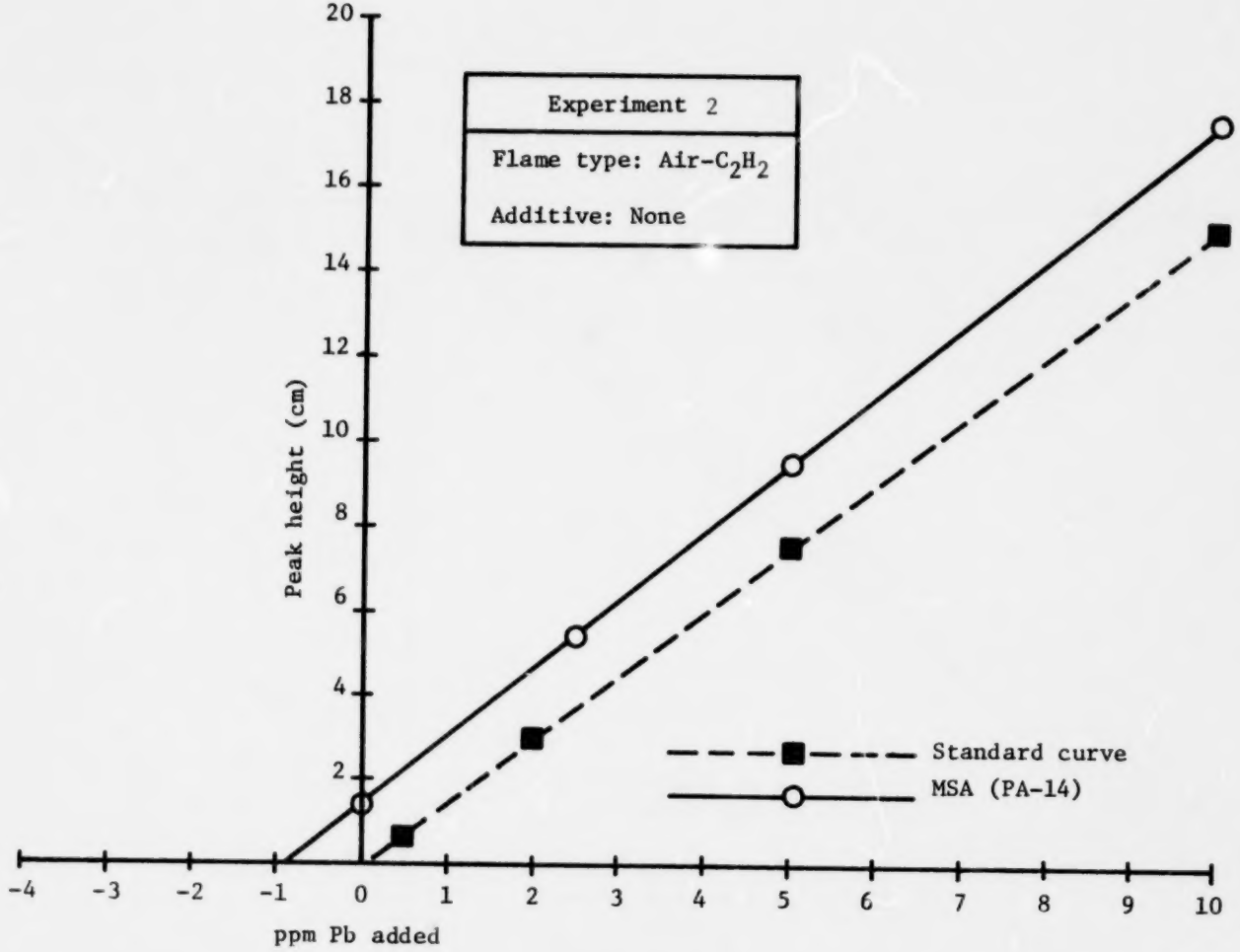


Figure 34. MSA plot for lead - Experiment 2.

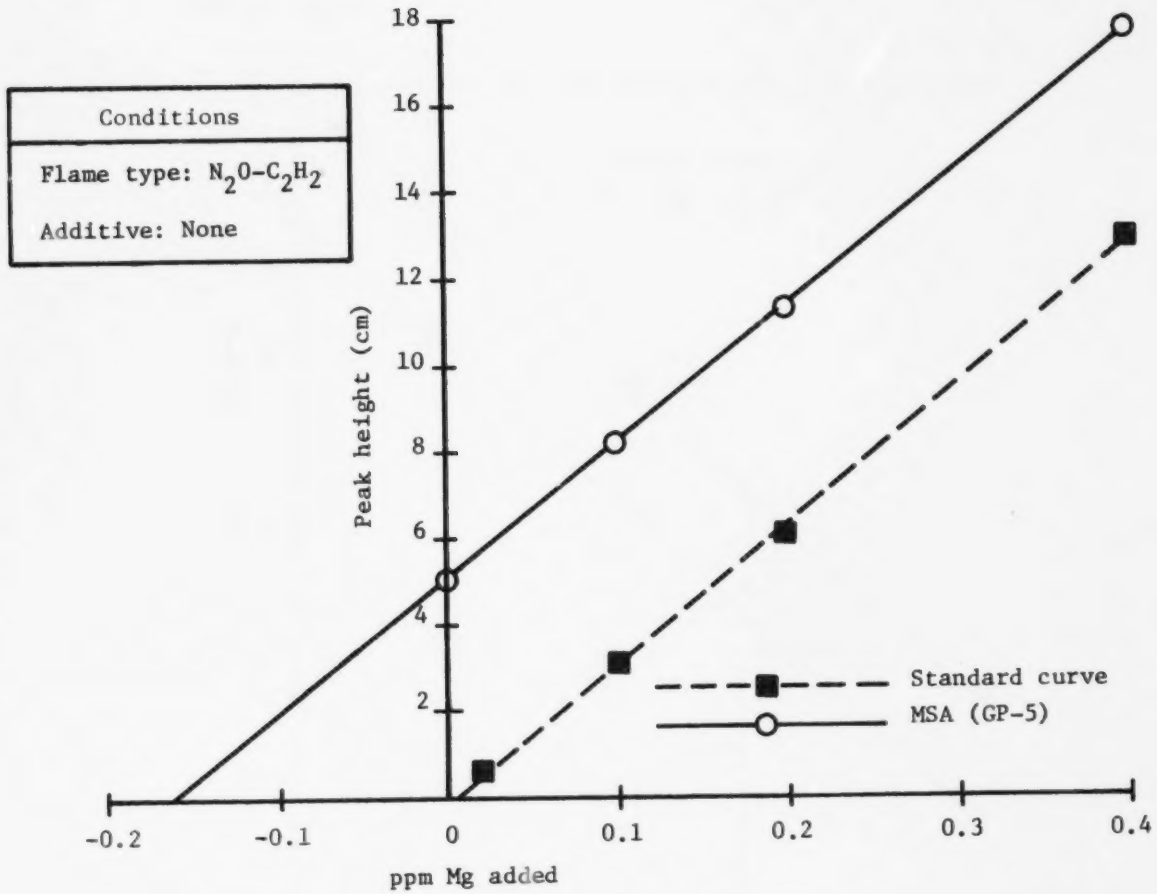


Figure 35. MSA plot for magnesium.

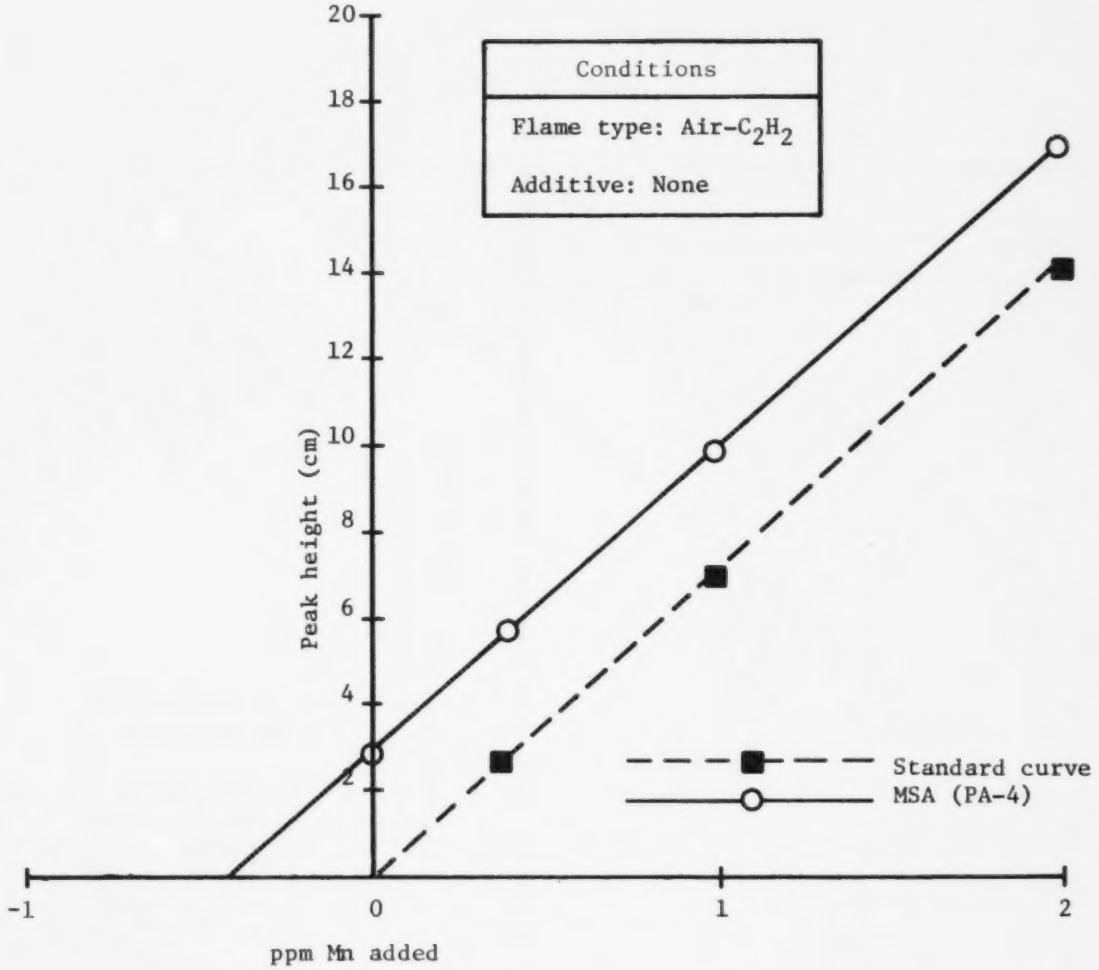


Figure 36. MSA plot for manganese.

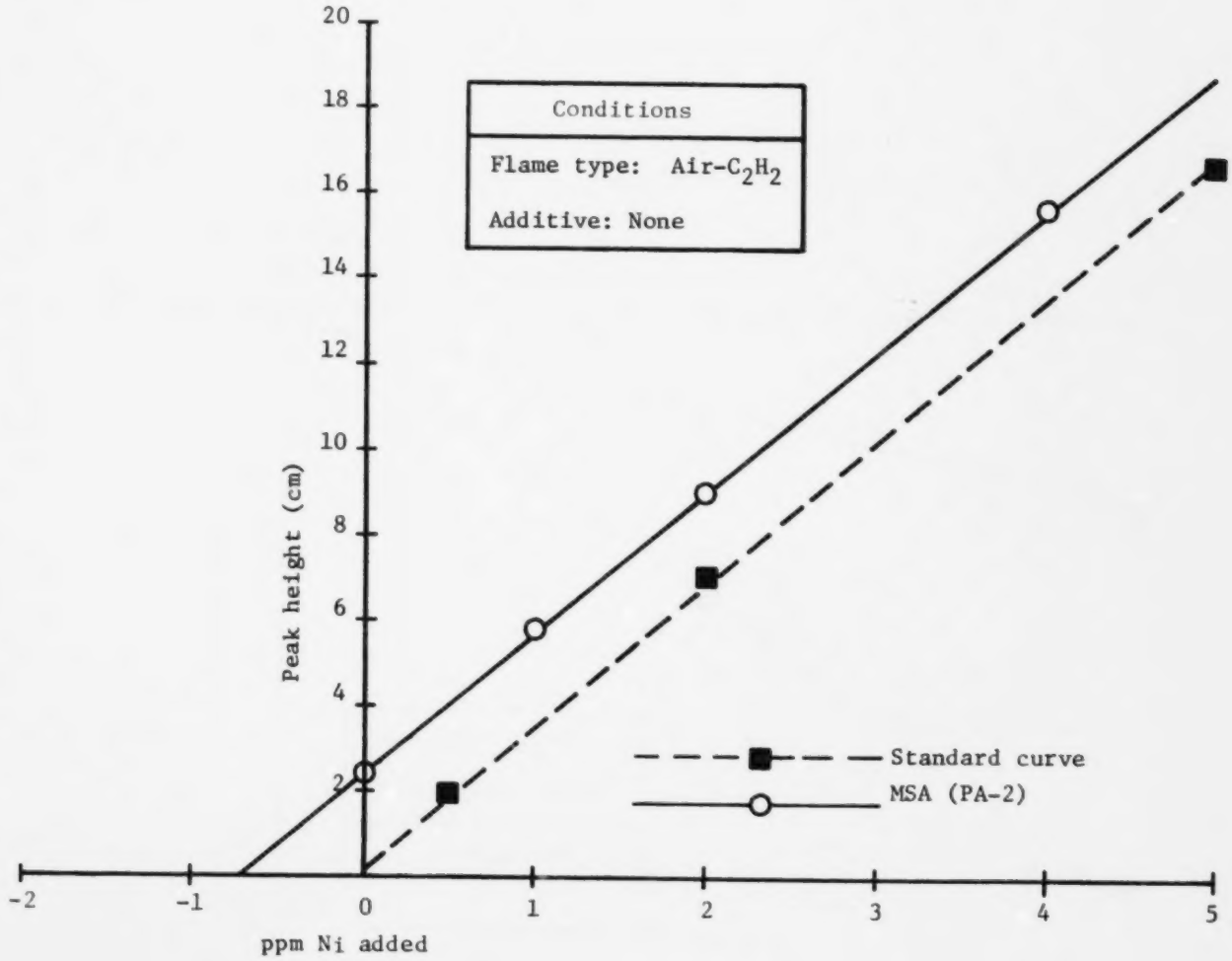


Figure 37. MSA plot for nickel.

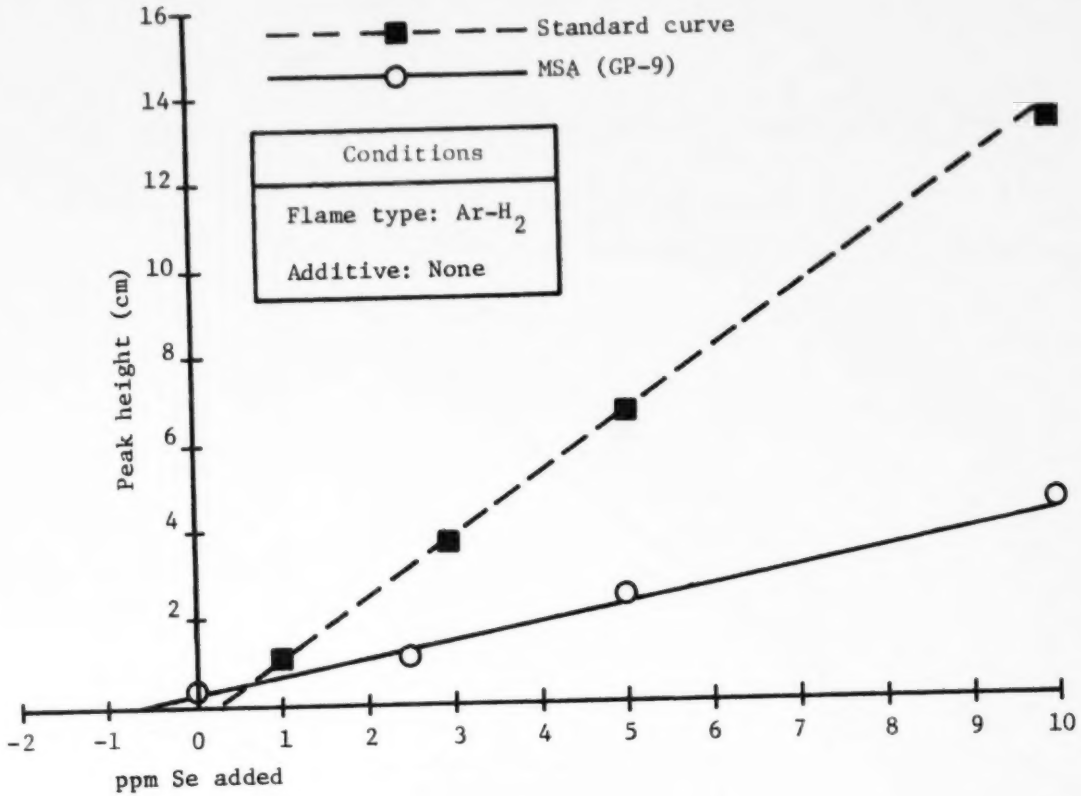


Figure 38. MSA plot for selenium.

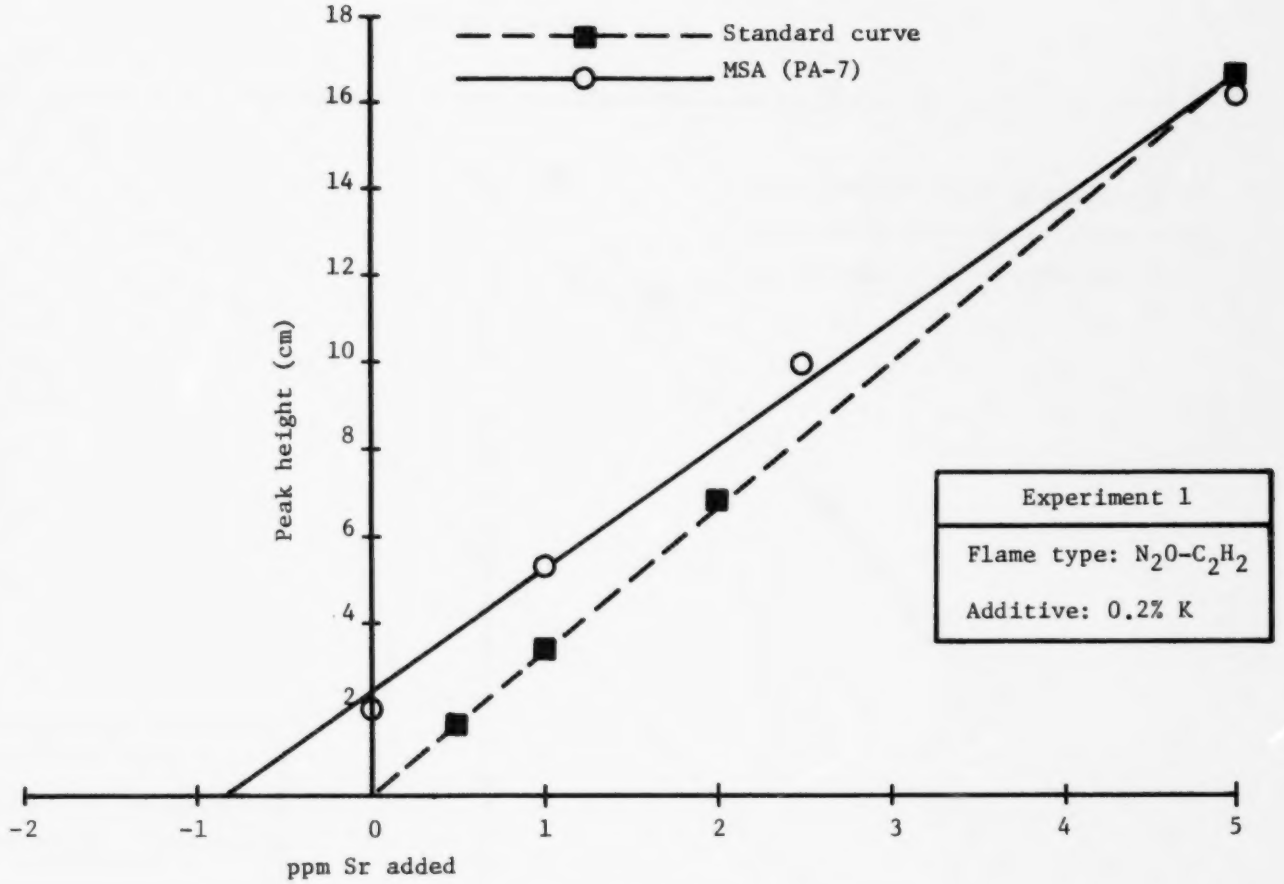


Figure 39. MSA plot for strontium - Experiment 1.

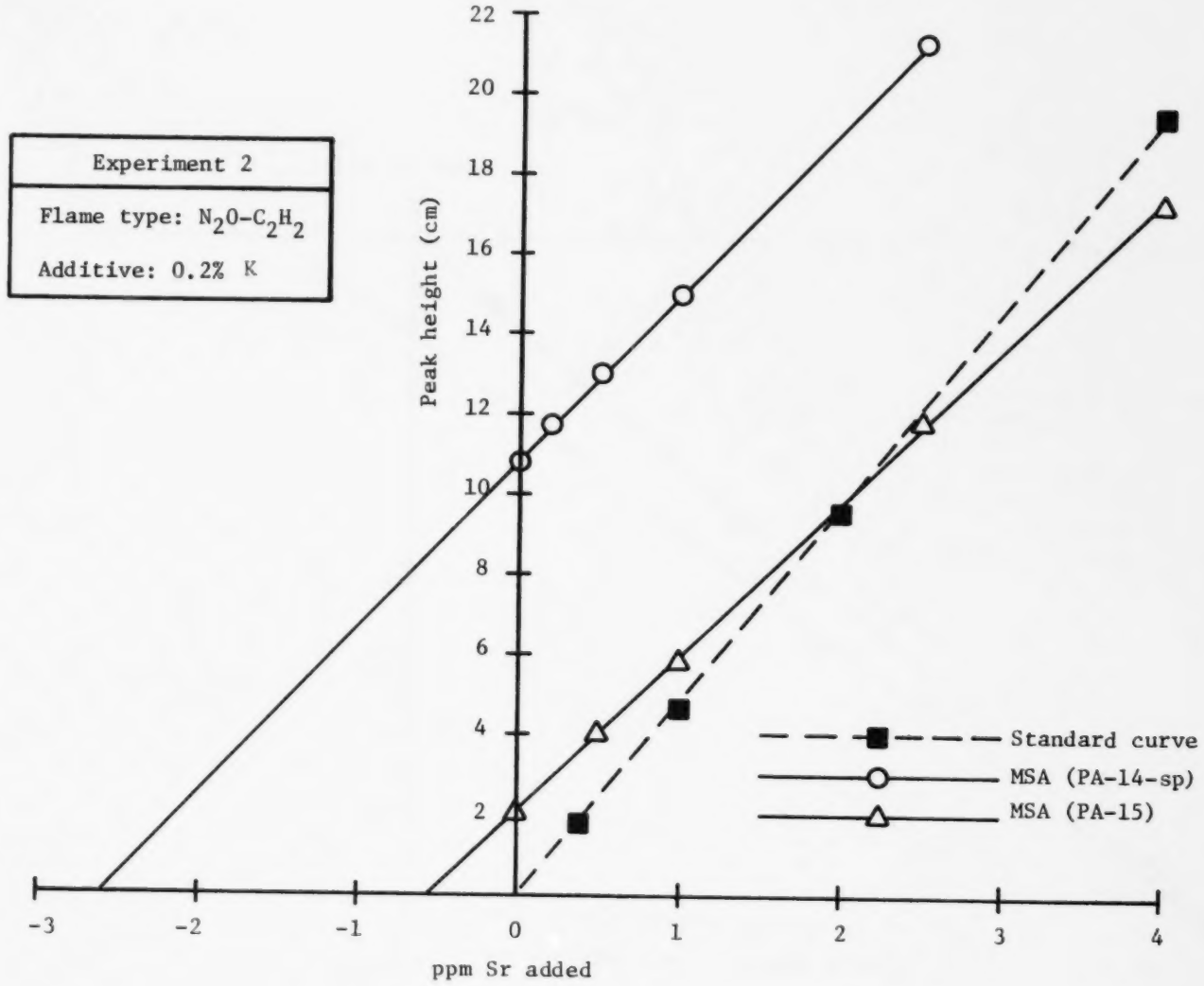


Figure 40. MSA plot for strontium - Experiment 2.

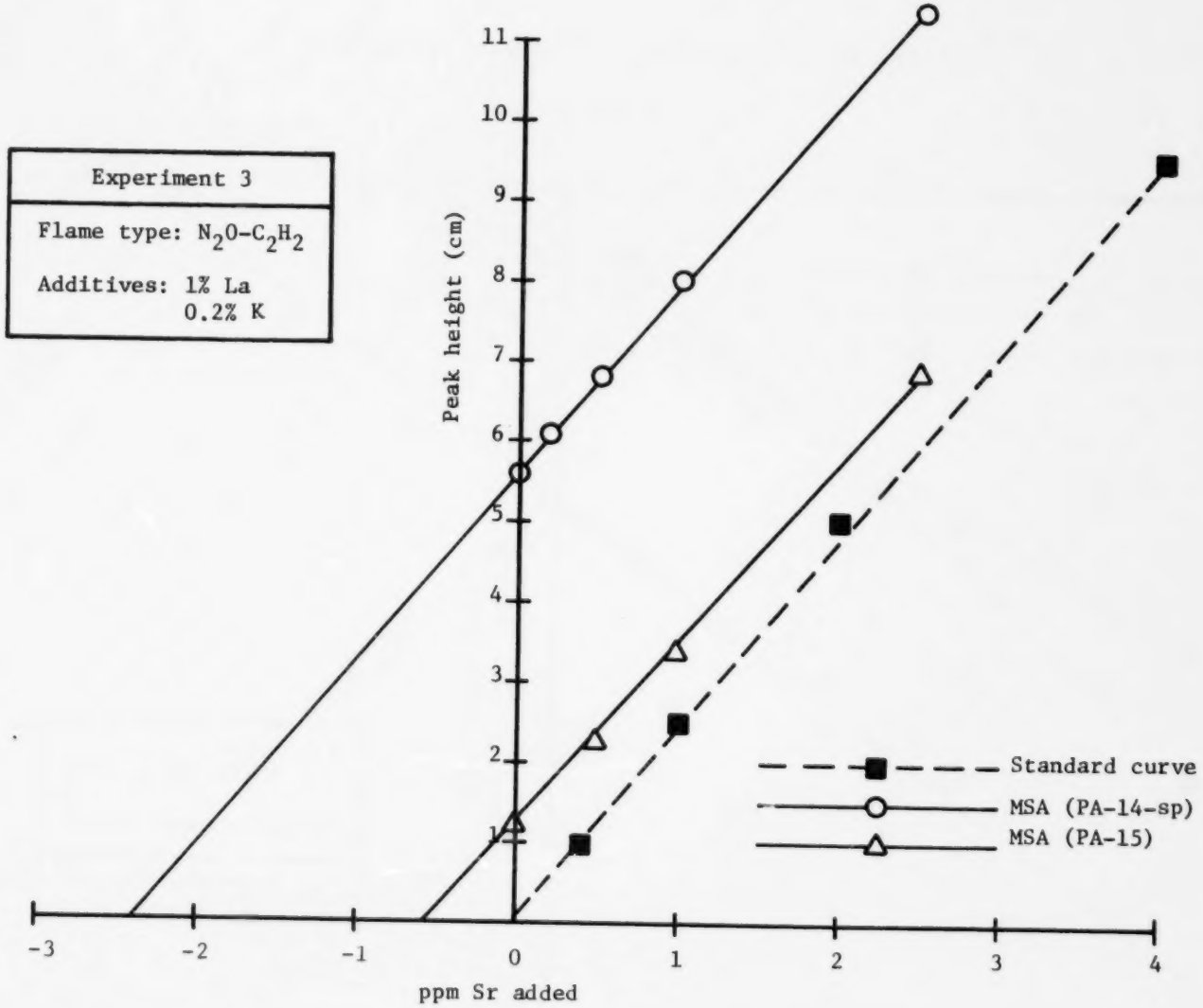


Figure 41. MSA plot for strontium - Experiment 3.

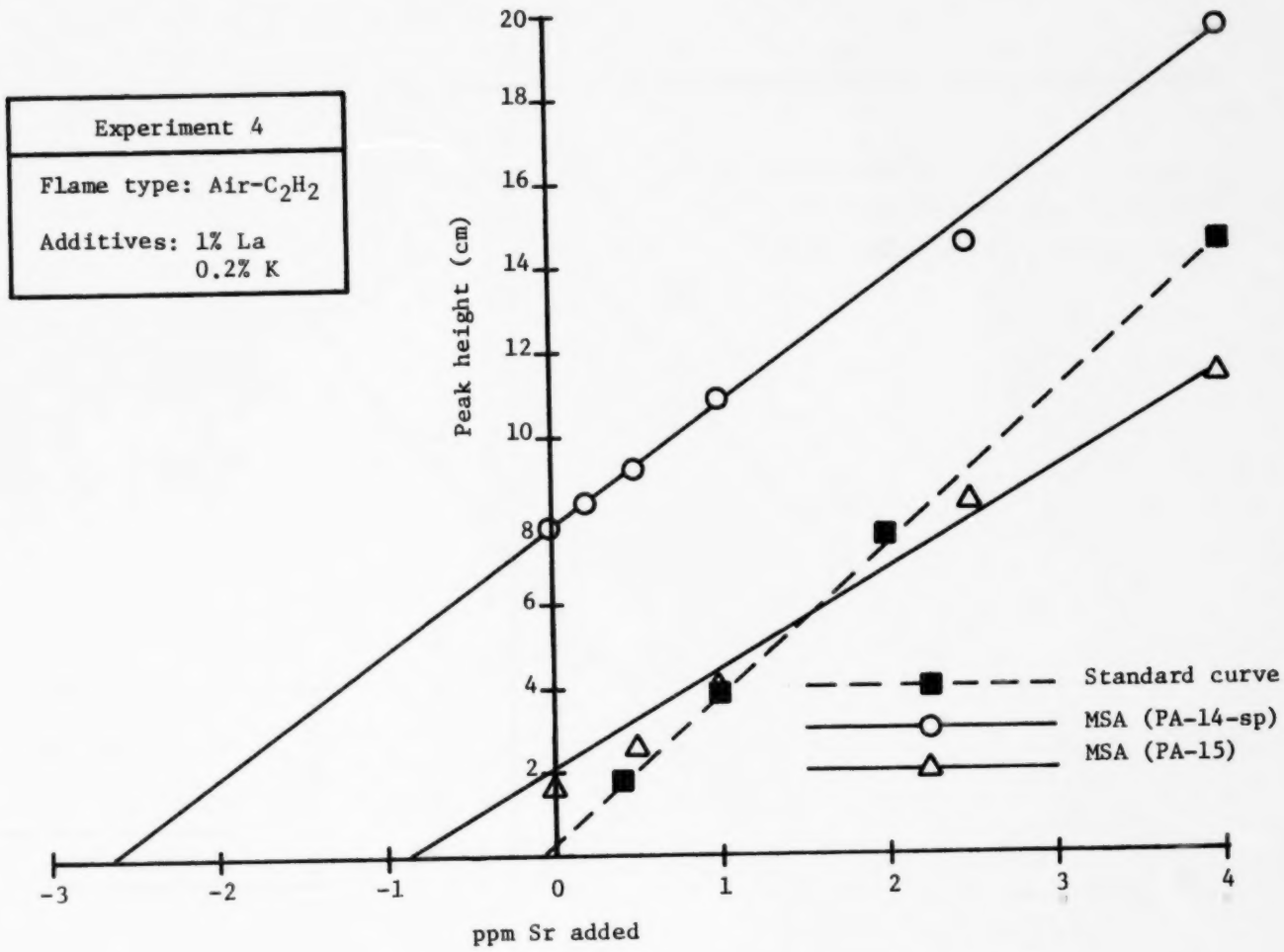


Figure 42. MSA plot for strontium - Experiment 4.

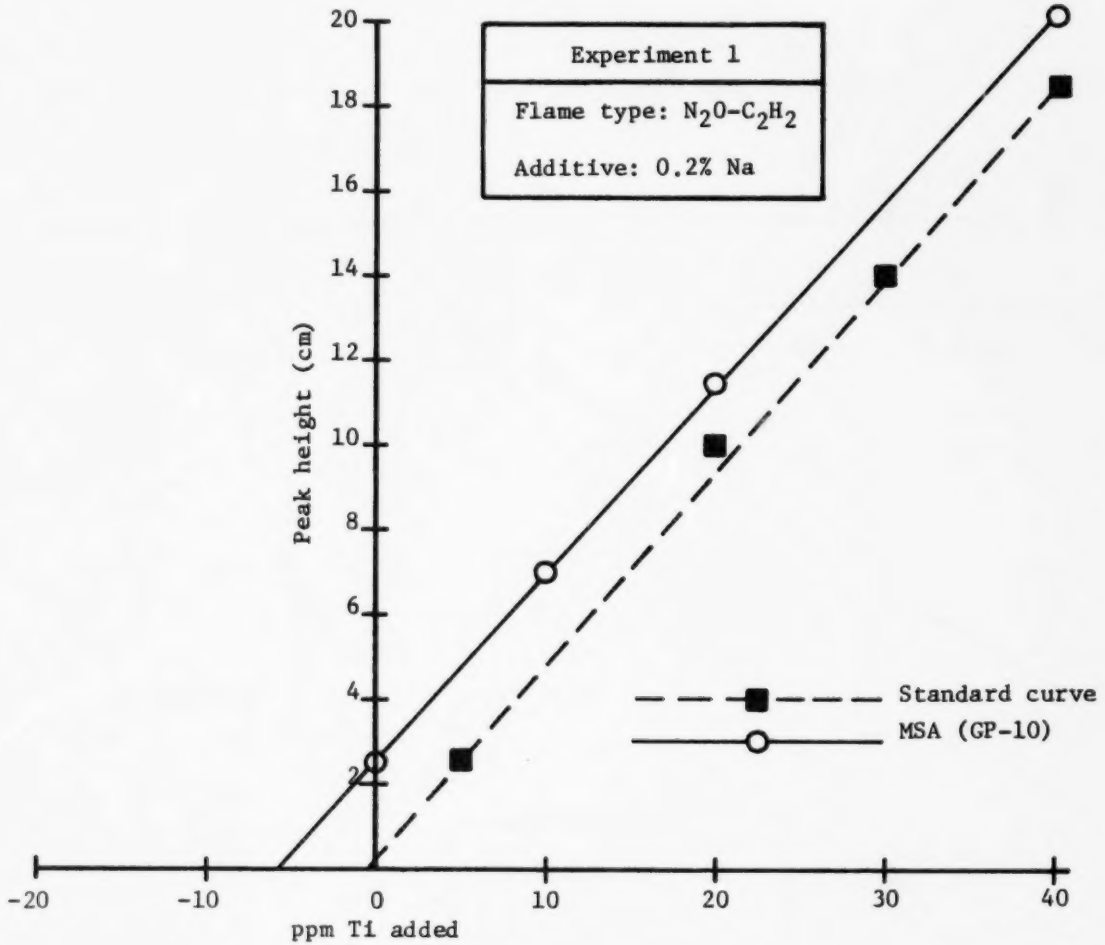


Figure 43. MSA plot for titanium - Experiment 1.

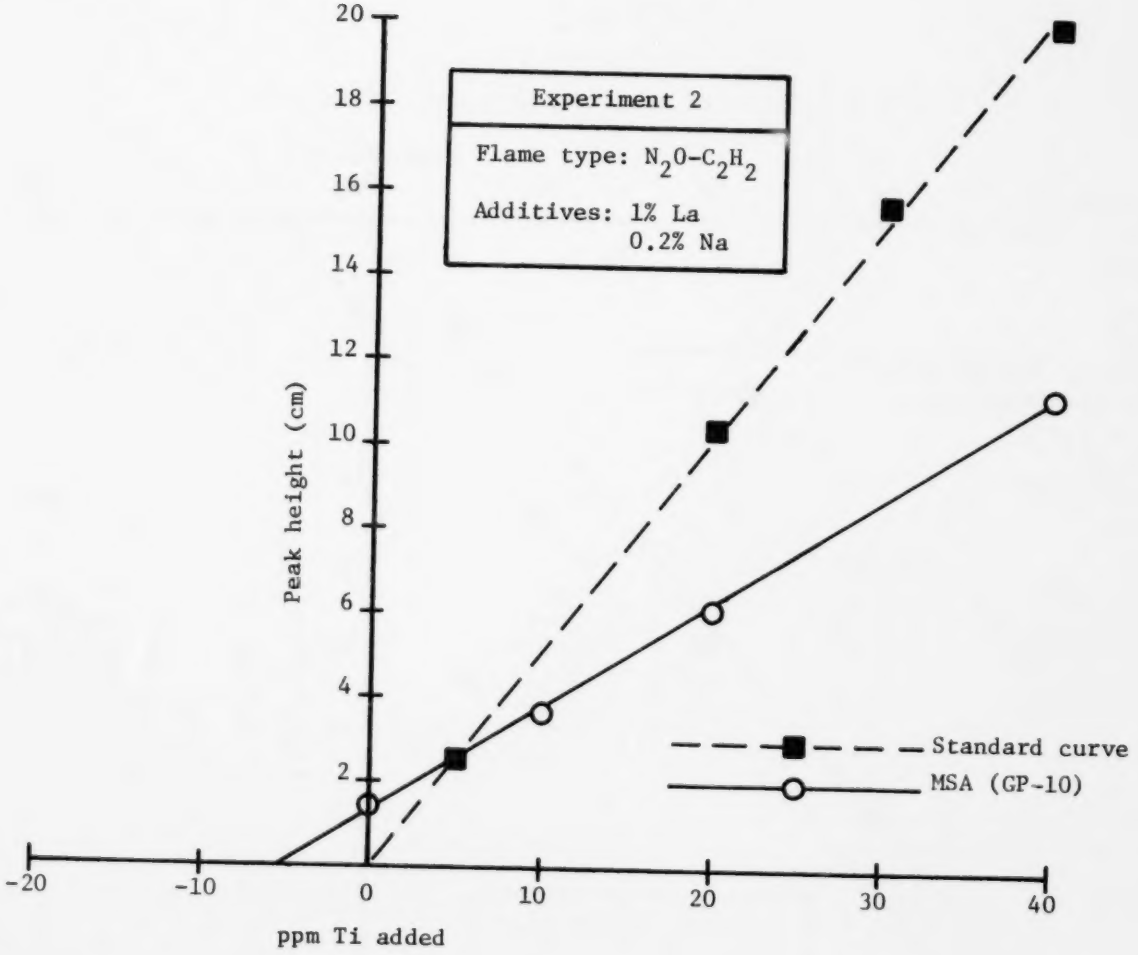


Figure 44. MSA plot for titanium - Experiment 2.

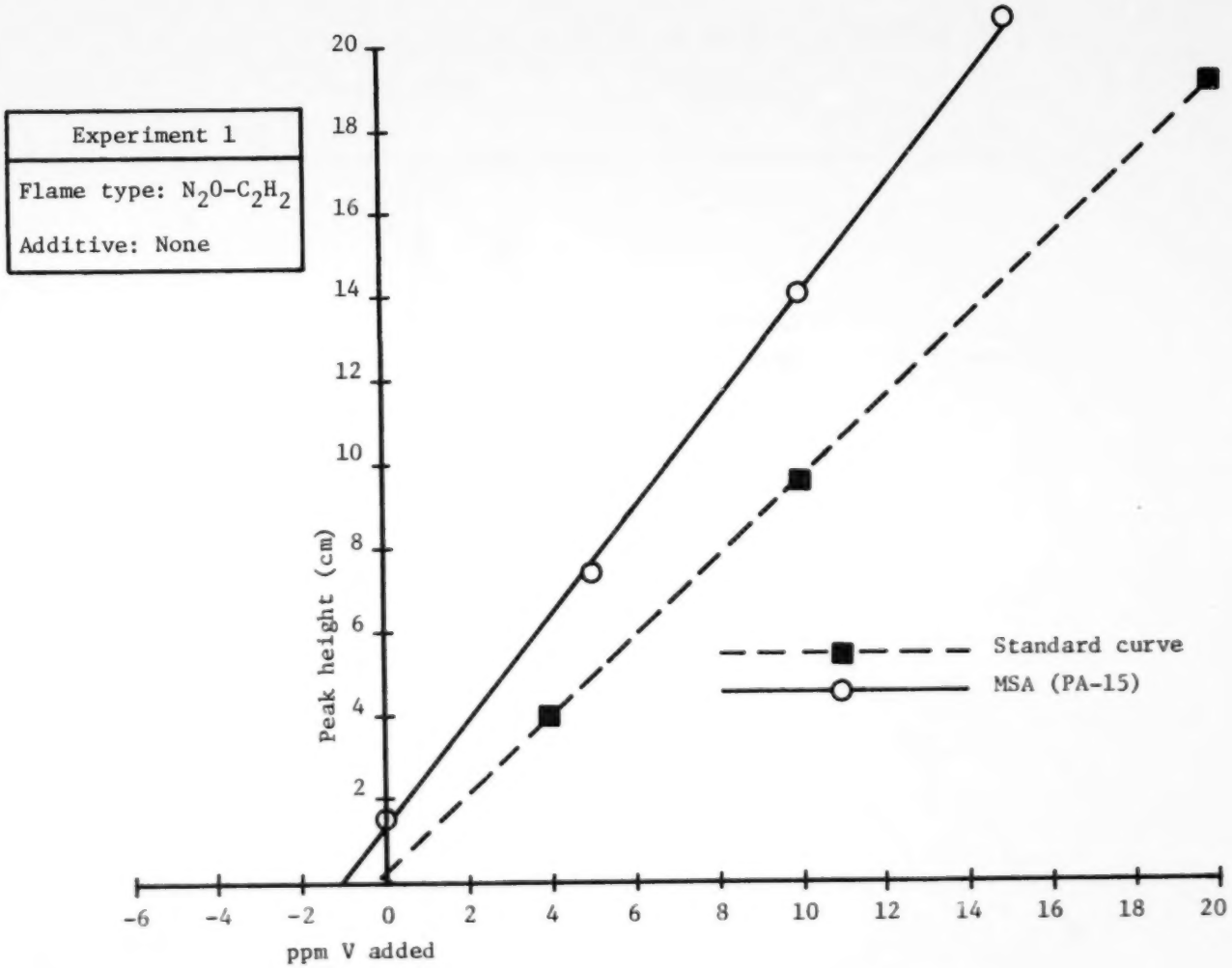


Figure 45. MSA plot for vanadium - Experiment 1.

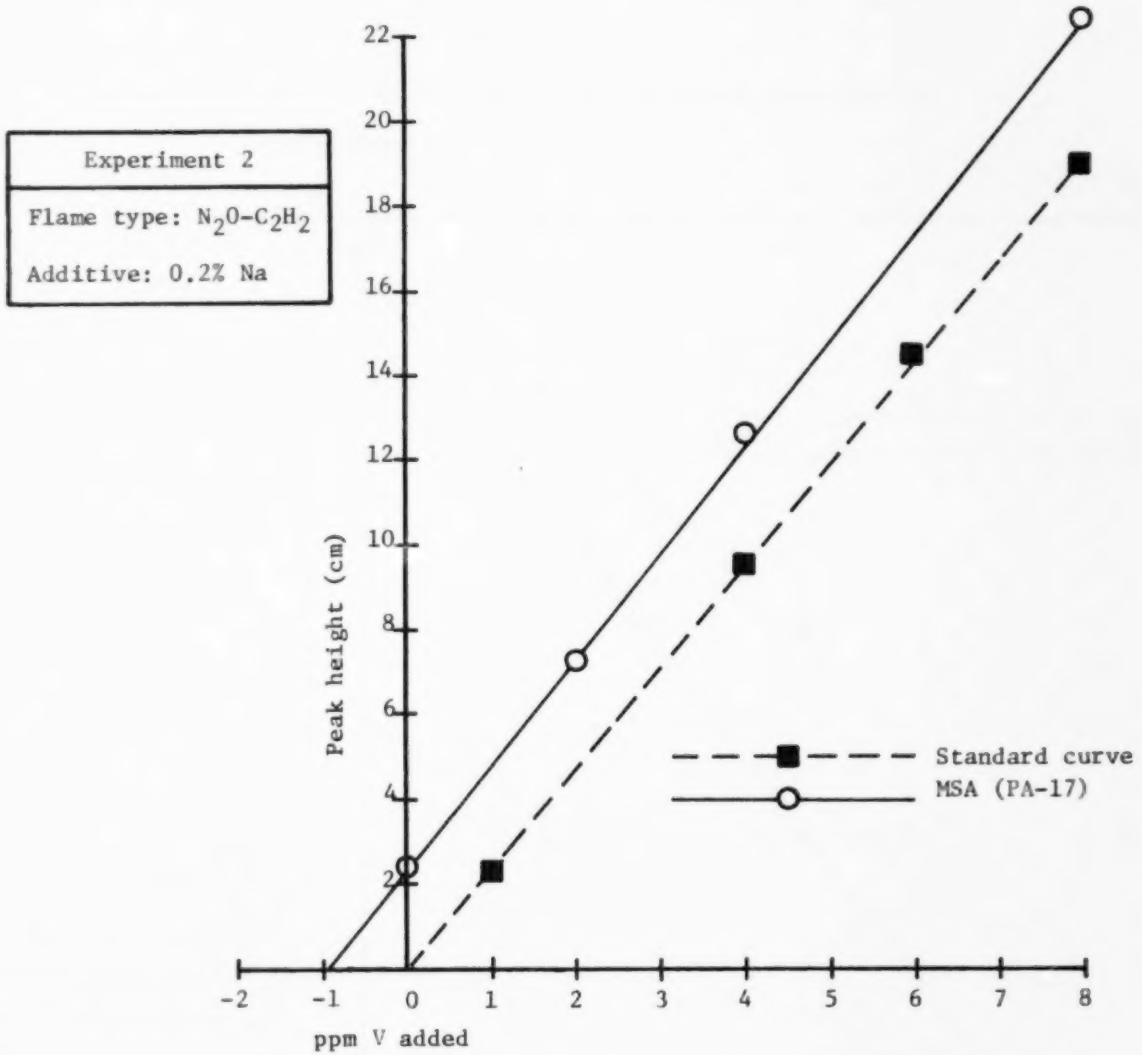


Figure 46. MSA plot for vanadium - Experiment 2.

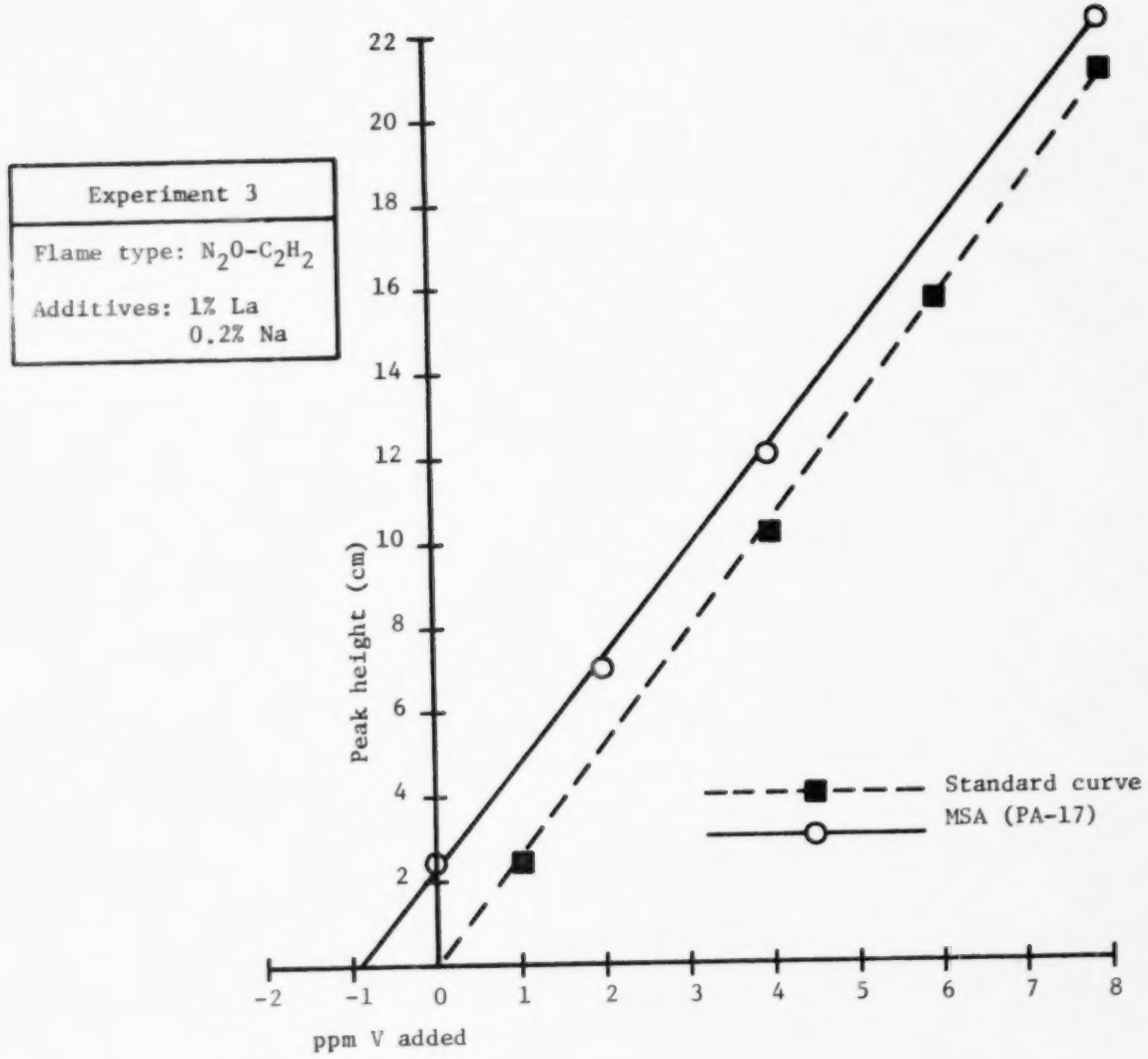


Figure 47. MSA plot for vanadium - Experiment 3.

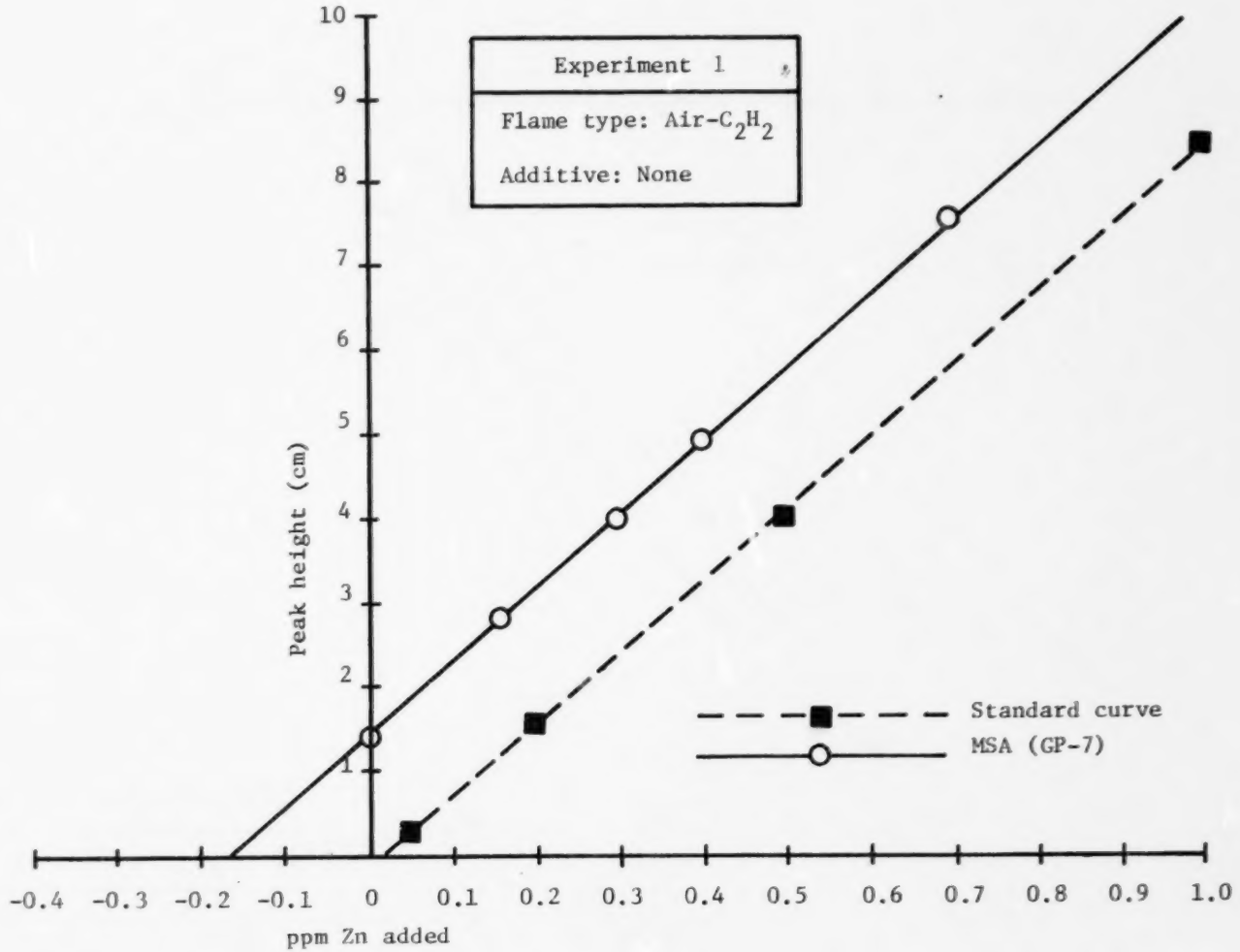


Figure 48. MSA plot for zinc - Experiment 1.

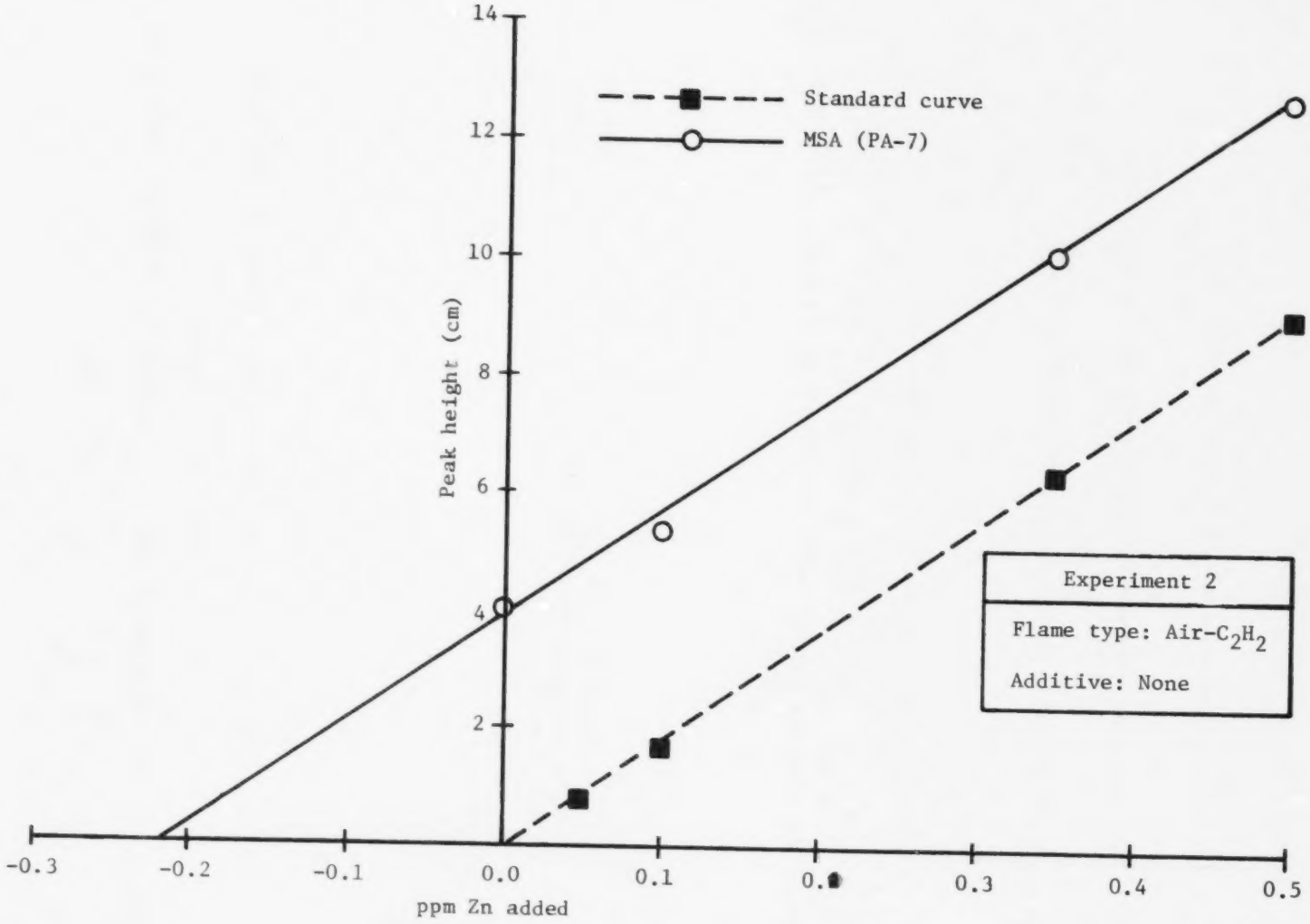


Figure 49. MSA plot for zinc - Experiment 2.

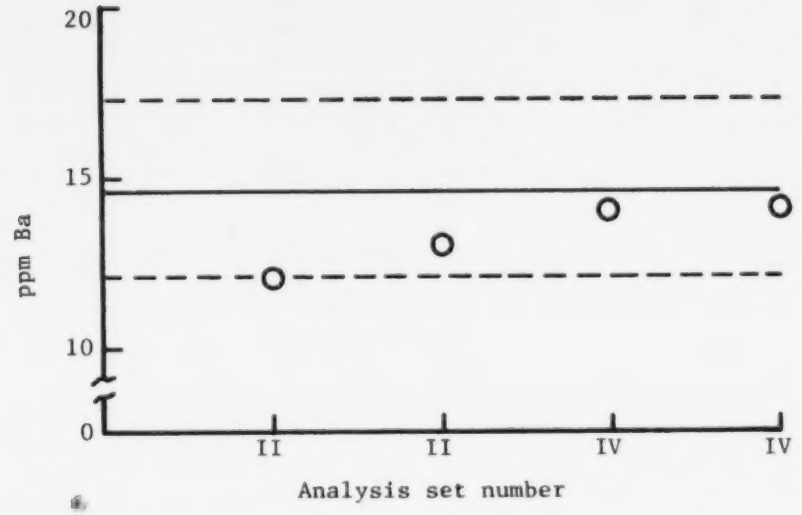


Figure 50. Quality control chart for barium in reference sediment B.

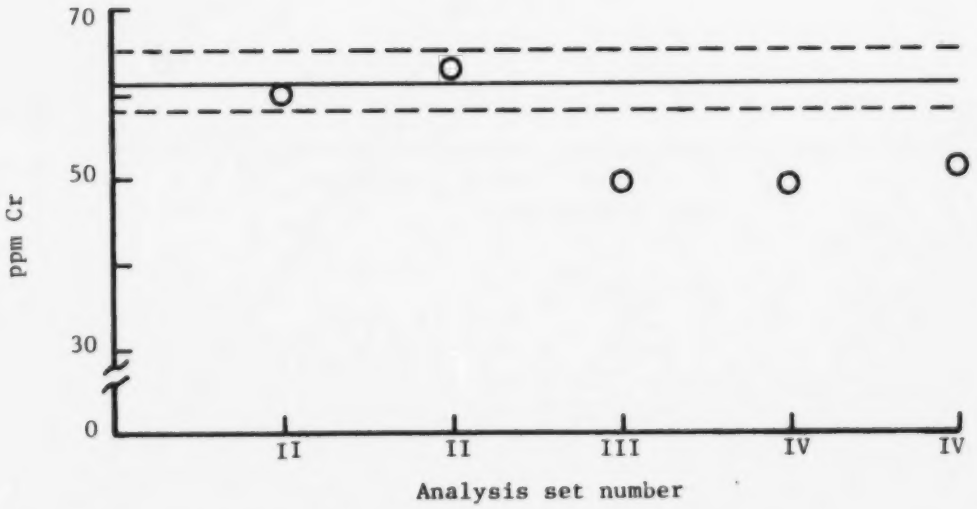


Figure 51. Quality control chart for chromium in reference sediment B.

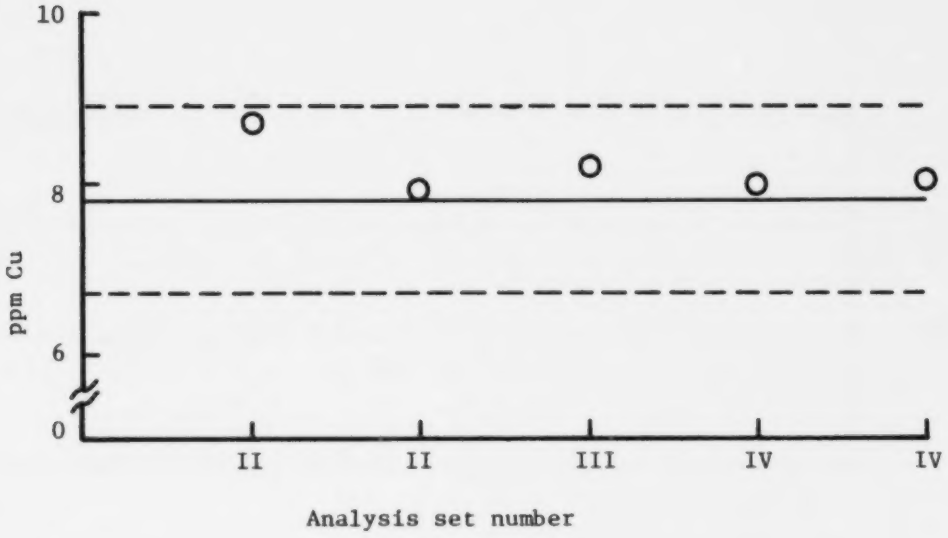


Figure 52. Quality control chart for copper in reference sediment B.

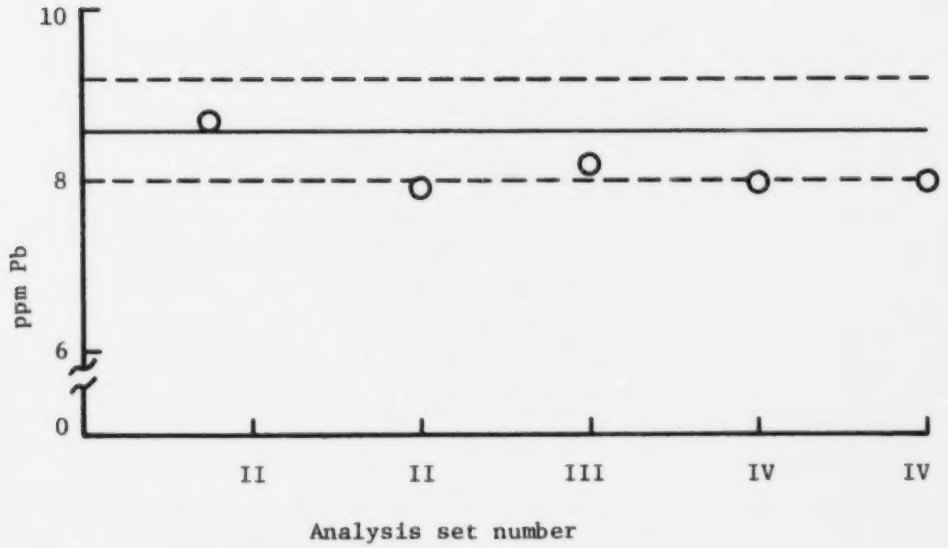


Figure 53. Quality control chart for lead in reference sediment B.

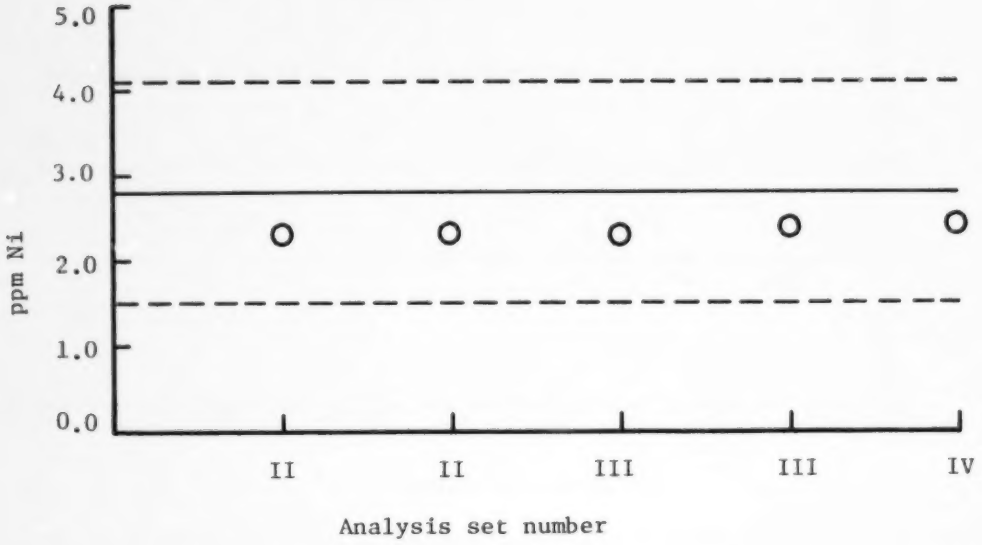


Figure 54. Quality control chart for nickel in reference sediment B.

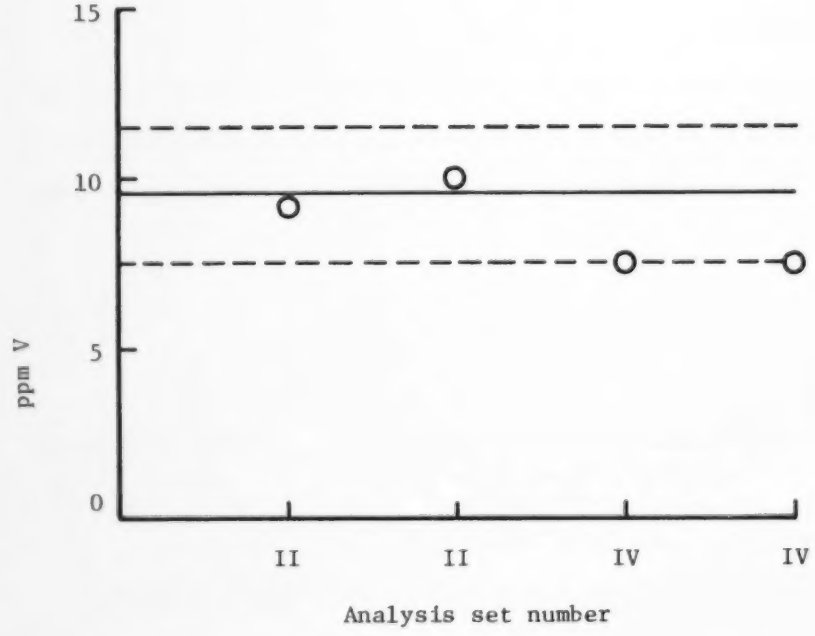


Figure 55. Quality control chart for vanadium in reference sediment B.

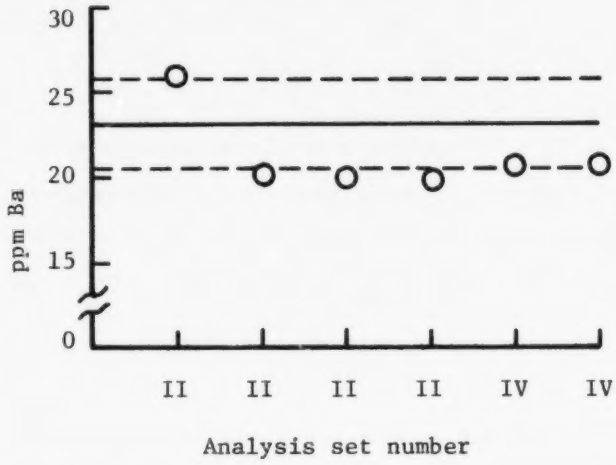


Figure 56. Quality control chart for barium in reference sediment C.

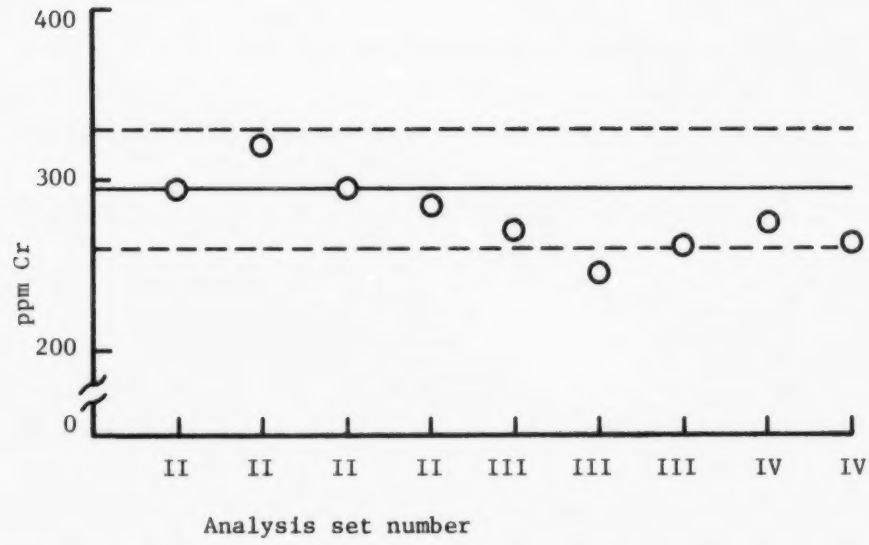


Figure 57. Quality control chart for chromium in reference sediment C.

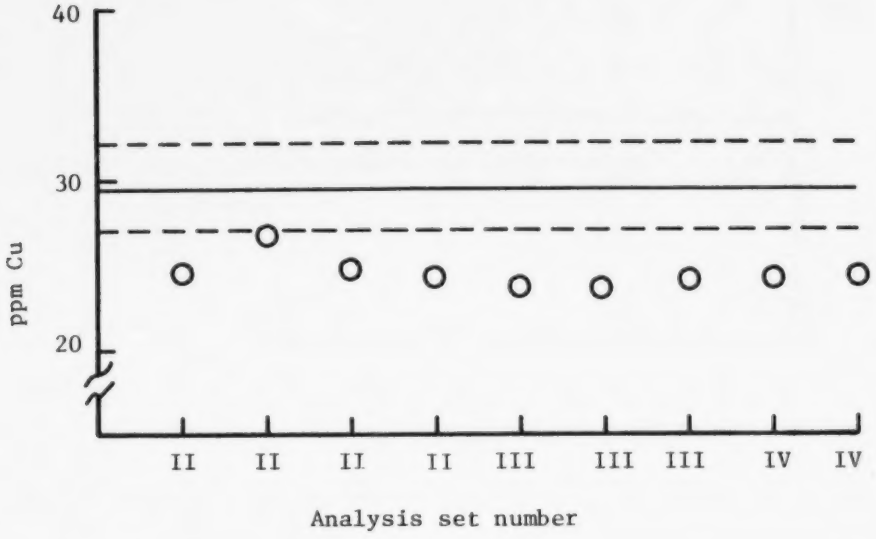


Figure 58. Quality control chart for copper in reference sediment C.

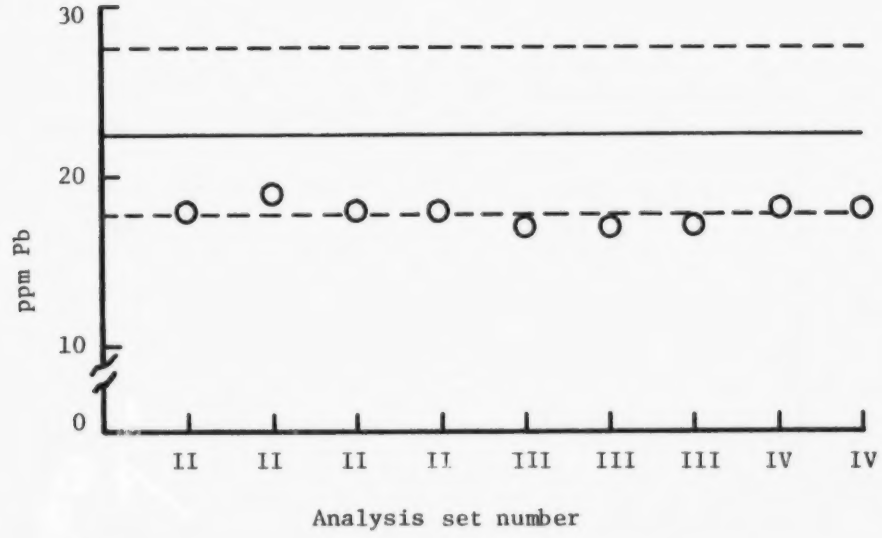


Figure 59. Quality control chart for lead in reference sediment C.

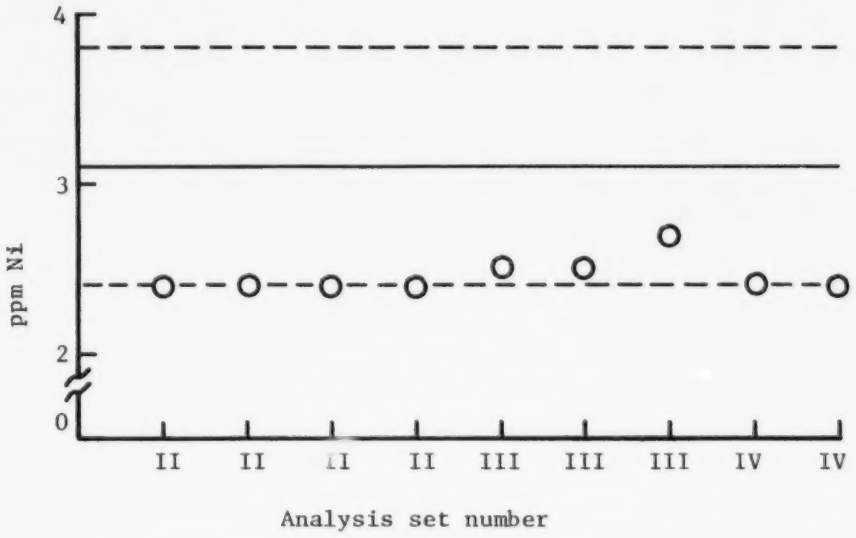


Figure 60. Quality control chart for nickel in reference sediment C.

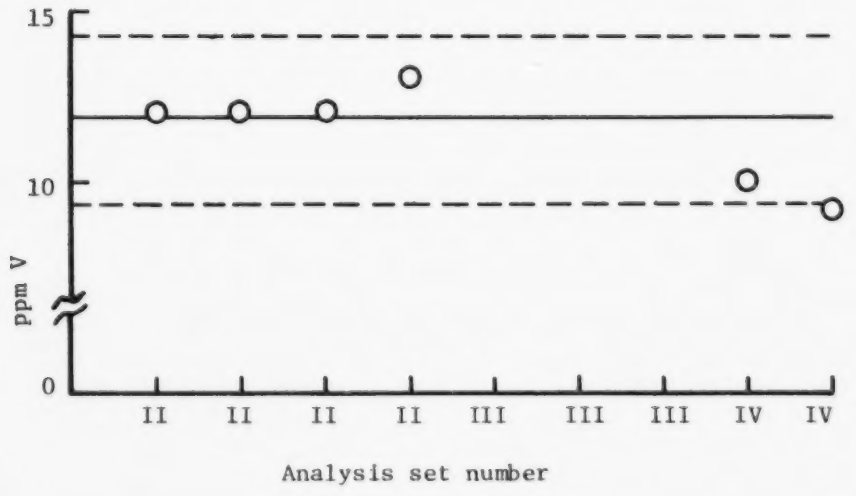


Figure 61. Quality control chart for vanadium in reference sediment C.

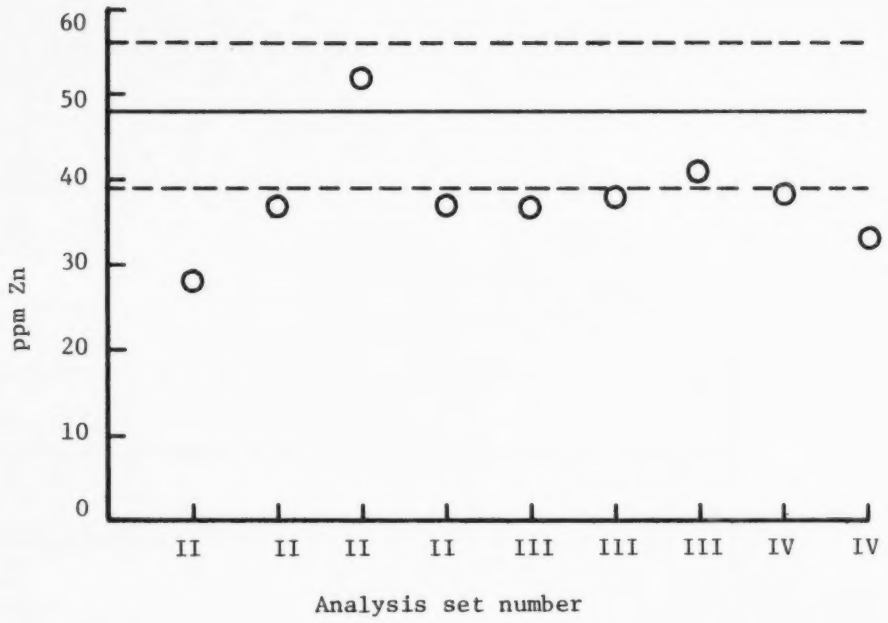


Figure 62. Quality control chart for zinc in reference sediment C.

TABLE 1. SAMPLE LOG FOR SEDIMENT (PA) SAMPLES

GSRI Sample I.D.	Sample Description
PA-1	West Branch Clarion River
PA-2	East Branch Clarion River
PA-3	Clarion River at Johnsonburg, Pa.
PA-4	Clarion River at Ridgway, Pa.
PA-5	Clarion River below Ridgway, Pa.
PA-6	Toby Creek at mouth
PA-7	Toby Creek 1-1/2 miles above mouth
PA-8	Toby Creek 2 miles upstream of Empire Tunnel
PA-9	Toby Creek upstream of Bliss Run
PA-10	Toby Creek at Brockway at 219 Highway Bridge
PA-11	Clarion River at Callen Run Footbridge
PA-12	Clarion River at Belltown Highway Bridge
PA-13	Clarion River upstream of Church Run and Footbridge
PA-14	Clarion River at Maxwell Run Ford
PA-15	Clarion River at Arroyo Ford Bridge
PA-16	Clarion River at Route 899 Bridge
PA-17	Clarion River at Route 36 Bridge at Cooksburg, Pa.

TABLE 2. SAMPLE LOG FOR SOIL (GP) SAMPLES

GSRI Sample I.D.	Sample Description
GP-1	Latitude 30°27'01"N. Longitude 89°02'13"W.
GP-2	Latitude 30°27'22"N. Longitude 89°02'21"W.
GP-3	Latitude 30°27'31"N. Longitude 89°02'26"W.
GP-4	Latitude 30°27'48"N. Longitude 89°02'30"W.
GP-5	Latitude 30°28'23"N. Longitude 89°02'45"W.
GP-6	Latitude 30°28'40"N. Longitude 89°02'53"W.
GP-7	Latitude 30°28'57"N. Longitude 89°02'51"W.
GP-8	Latitude 30°29'06"N. Longitude 80°03'02"W.
GP-9	Latitude 30°29'14"N. Longitude 89°03'07"W.
GP-10	Latitude 30°29'15"N. Longitude 89"03"36"W.
GP-11	Latitude 30°28'52"N. Longitude 89"04'07"W.
GP-12	Latitude 30°28'32"N. Longitude 89°04'06"W.
GP-13	Latitude 30°27"42"N. Longitude 89°04'05"W.
GP-14	Latitude 30°27'21"N. Longitude 89°04'17"W.
GP-15	One mile north of I-10 near Pass Christian, Long Beach exit.
GP-16	One mile north of I-10 near Pass Christian, Long Beach exit.
GP-17	Between Kiln and I-10 near I-10 Kiln exit.
GP-18	One hundred yards north of I-10 and one mile east of NASA I-10 exit.
GP-19	One mile north of I-10 NASA exit, east side of road.
GP-20	One mile south of I-10 NASA exit.

TABLE 3. CONDITIONS USED FOR INITIAL ANALYSIS OF SOIL (GP) AND SEDIMENT (PA) SAMPLES

Element	Wavelength (nm)	Spectral Band (nm)	Flame Type	Comments	Detection Limit (ppm)
Ag	328.1	0.7	Air-C_2H_2		1.3
Al	309.3	0.7	N_2O-C_2H_2		5
As	193.7	0.7	Argon-H_2		6
Ba	553.6	0.4	N_2O-C_2H_2	Add 0.2% potassium or sodium to all solutions	6
Be	234.9	0.7	N_2O-C_2H_2		0.4
Bi	223.1	0.7	Air-C_2H_2		6
Ca	422.7	1.4	Air-C_2H_2		2
Cd	228.8	0.7	Air-C_2H_2		0.3
Co	240.7	0.2	Air-C_2H_2		3.0
Cr	357.9	0.7	N_2O-C_2H_2		2
Cu	324.8	0.7	Air-C_2H_2		0.6
Fe	248.3	0.2	Air-C_2H_2		2
K	766.5	1.4	Air-C_2H_2		1.5
Mg	285.2	0.7	N_2O-C_2H_2		0.3
Mn	279.5	0.2	Air-C_2H_2		0.5
Mo	313.3	0.7	N_2O-C_2H_2		6.3
Na*	589.0	1.4	Air-C_2H_2		0.2
Ni	232.0	0.2	Air-C_2H_2	Use 4-inch single slot burner head	6
Pb	283.3	0.7	Air-C_2H_2		4.0
Sb	217.6	0.2	Air-C_2H_2		25
Se	196.0	0.7	Argon-H_2		2.5
Sn	286.3	0.7	Air-C_2H_2		25
Sr	460.7	1.4	N_2O-C_2H_2	Add 0.2% potassium or sodium to all solutions	1.5
Ti	365.3	0.2	N_2O-C_2H_2	Add 0.2% potassium or sodium to all solutions	25
V	318.4	0.7	N_2O-C_2H_2		6.0
Zn	213.9	0.7	Air-C_2H_2		0.7

*Analysis was done by atomic emission

TABLE 4. AAS ANALYSIS OF MATRIX CONSTITUENTS IN SOIL (GP) SAMPLES

Sample	% Al	ppm Ca	% Fe	ppm K	ppm Mg	ppm Na	% PO_4
GP-1	0.141	<2.0	0.105	102	163	23.1	0.032
GP-2	0.500	<2.0	0.444	144	143	13.8	0.037
GP-3	0.304	4.1	0.490	103	103	18.1	0.043
GP-4	0.427	3.5	0.352	139	174	15.1	0.043
GP-5	0.534	<2.0	0.380	143	137	23.2	0.031
GP-6	0.595	<2.0	0.347	106	111	12.6	0.017
GP-7	0.519	<2.0	0.408	173	155	20.0	0.026
GP-8	0.595	<2.0	0.493	131	164	28.5	0.048
GP-9	1.080	3.5	0.657	212	270	32.1	0.034
GP-10	0.830	22.0	0.876	152	184	30.3	0.045
GP-11	0.633	<2.0	0.437	836	119	36.0	0.016
GP-12	0.472	<2.0	0.284	97	133	17.1	0.030
GP-13	0.589	31.9	0.448	166	275	22.5	0.22
GP-14	0.534	<2.0	0.383	70	95	0.3	0.017
GP-15	0.469	<2.0	0.307	73	76	14.0	0.018
GP-16	0.215	<2.0	0.184	60	84	20.9	0.018
GP-17	0.397	<2.0	0.264	99	148	18.5	0.019
GP-18	0.455	4.8	0.263	104	155	19.6	0.022
GP-19	0.658	7.9	0.201	241	255	180	0.069
GP-20	0.828	9.8	0.789	263	288	26.0	0.030

TABLE 5. AAS ANALYSIS OF TRACE METAL CONCENTRATIONS IN SOIL (GP) SAMPLES

Sample	ppm Ag	ppm As	ppm Be	ppm Bi	ppm Cd	ppm Co	ppm Cr	ppm Cu
GP-1	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	4.1	1.6
GP-2	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	4.7	1.7
GP-3	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	4.3	1.9
GP-4	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	5.4	2.2
GP-5	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	6.4	2.1
GP-6	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	6.8	1.8
GP-7	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	5.8	2.2
GP-8	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	6.6	2.1
GP-9	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	10.7	1.9
GP-10	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	18.9	4.0
GP-11	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	6.9	1.3
GP-12	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	4.1	0.7
GP-13	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	9.4	2.9
GP-14	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	4.1	2.7
GP-15	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	2.0	1.2
GP-16	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	2.5	0.6
GP-17	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	6.6	0.7
GP-18	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	10.9	0.7
GP-19	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	6.6	1.6
GP-20	<1.3	<6.0	<0.4	<6.0	<0.3	<3.0	15.0	2.9

(continued)

TABLE 5 (continued).

Sample	ppm Ni	ppm Pb	ppm Sb	ppm Se	ppm Sn	ppm Ti	ppm Zn
GP-1	<6	7.3	<25	<2.5	<25	211	9.3
GP-2	<6	6.6	<25	8.9	<25	98	11.6
GP-3	<6	11.9	<25	7.2	<25	57	9.4
GP-4	<6	9.3	<25	7.7	<25	72	22.3
GP-5	<6	12.7	<25	9.9	<25	162	10.4
GP-6	<6	6.7	<25	4.5	<25	163	8.4
GP-7	<6	8.1	<25	9.9	<25	195	11.1
GP-8	<6	10.1	<25	<2.5	<25	201	9.5
GP-9	<6	12.7	<25	9.0	<25	243	11.6
GP-10	<6	12.4	<25	10.8	<25	129	11.6
GP-11	<6	4.1	<25	10.0	<25	147	5.7
GP-12	<6	6.8	<25	<2.5	<25	175	5.7
GP-13	<6	7.2	<25	6.2	<25	71	149
GP-14	<6	7.0	<25	9.9	<25	111	6.3
GP-15	<6	7.9	<25	<2.5	<25	87	5.1
GP-16	<6	8.0	<25	9.9	<25	61	5.0
GP-17	<6	8.0	<25	8.9	<25	98	5.8
GP-18	<6	4.3	<25	6.3	<25	149	5.7
GP-19	<6	15.0	<25	6.3	<25	65	9.7
GP-20	<6	15.3	<25	9.0	<25	242	9.9

TABLE 6. AAS ANALYSIS OF MATRIX CONSTITUENTS IN SEDIMENT (PA) SAMPLES

Sample	% Al	ppm Ca	% Fe	ppm K	ppm Mg	ppm Na	% PO_4
PA-1	0.477	70.5	2.68	685	440	112	0.10
PA-2	0.686	57.4	2.95	642	483	82.0	*
PA-3	0.321	10.4	5.31	303	282	87.9	0.10
PA-4	0.630	122	3.81	541	462	132	0.11
PA-5	0.356	5.0	7.83	376	206	129	0.19
PA-6	0.496	288	3.96	481	632	122	0.11
PA-7	0.500	254	3.89	461	608	123	0.11
PA-8	0.369	12.3	3.06	362	267	209	0.09
PA-9	0.420	3.6	5.25	330	348	51.5	0.14
PA-10	0.544	502	6.90	513	447	76.5	0.18
PA-11	0.381	38.0	2.41	494	286	205	0.23
PA-12	0.927	5830	7.60	696	1780	70.9	0.23
PA-13	1.03	51.3	5.60	753	1380	50.0	0.16
PA-14	0.396	25.7	2.45	343	308	64.9	0.11
PA-15	0.840	3.1	10.6	605	854	67.0	0.34
PA-16	0.924	22.9	6.17	889	997	88.4	0.34
PA-17	0.926	4.1	5.30	622	1260	68.7	0.17

*Sample size insufficient for analysis.

TABLE 7. AAS ANALYSIS OF TRACE CONSTITUENTS IN SEDIMENT (PA) SAMPLES

Sample	ppm Ag	ppm Ba	ppm Be	ppm Cd	ppm Co	ppm Cr	ppm Cu
PA-1	<1.3	68	0.7	<0.3	8.9	8.6	10.5
PA-2	<1.3	44	0.8	<0.3	20.9	11.0	10.9
PA-3	<1.3	35	1.2	<0.3	12.2	13.6	8.5
PA-4	<1.3	56	1.0	<0.3	12.0	7.2	32.7
PA-5	<1.3	30	1.7	<0.3	18.3	10.4	12.9
PA-6	<1.3	54	1.0	<0.3	15.3	9.3	57.6
PA-7	<1.3	72	1.0	<0.3	15.8	13.1	48.0
PA-8	<1.3	31	1.2	<0.3	14.9	7.3	10.2
PA-9	<1.3	28	1.2	<0.3	15.7	12.8	16.2
PA-10	<1.3	117	1.1	<0.3	16.8	19.7	17.8
PA-11	<1.3	44	0.9	<0.3	13.0	1.3	9.0
PA-12	<1.3	177	1.2	<0.3	17.8	27.4	25.3
PA-13	<1.3	32	1.2	<0.3	15.5	21.5	21.9
PA-14	<1.3	55	1.0	<0.3	11.8	5.8	28.8
PA-15	<1.3	29	1.9	<0.3	20.5	25.8	25.9
PA-16	<1.3	29	1.8	<0.3	16.6	27.6	26.2
PA-17	<1.3	28	1.7	<0.3	14.2	12.7	29.3

(continued)

TABLE 7 (continued).

Sample	ppm Mn	ppm Mo	ppm Ni	ppm Pb	ppm Sr	ppm V	ppm Zn
PA-1	571	<6.3	15.8	28.8	5.3	12	128
PA-2	1890	<6.3	24.8	19.2	3.4	13	181
PA-3	931	<6.3	22.4	22.3	2.7	12	163
PA-4	562	<6.3	21.2	26.3	8.8	15	194
PA-5	990	<6.3	27.6	17.8	4.3	19	184
PA-6	787	<6.3	18.1	30.4	15.8	15	155
PA-7	850	<6.3	20.1	31.0	11.5	13	150
PA-8	991	<6.3	25.6	15.0	3.3	8.6	199
PA-9	1050	<6.3	19.4	17.3	4.7	18	199
PA-10	2040	<6.3	23.1	28.0	11.6	24	175
PA-11	1020	<6.3	26.5	13.9	3.4	6.5	192
PA-12	593	<6.3	61.1	28.7	26.7	27	192
PA-13	702	<6.3	20.8	22.1	7.7	30	140
PA-14	864	<6.3	16.8	24.4	8.5	12	183
PA-15	1100	<6.3	25.0	23.9	5.0	32	171
PA-16	798	<6.3	25.2	21.7	13.7	33	160
PA-17	627	<6.3	22.3	21.8	5.2	<6.0	159

TABLE 8. FIRST INTERFERENCE STUDY FOR THE ANALYSIS OF BARIUM*

ppm Ba	ppm Metal Added					Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Ca	Mn	Mg			
5	0	0	0	0	0	11.3	0.049	0
5	10	0	0	0	0	10.2	0.045	-10
5	50	0	0	0	0	8.5	0.038	-25
5	100	0	0	0	0	8.0	0.035	-29
5	500	0	0	0	0	7.3	0.032	-36
5	1000	0	0	0	0	6.3	0.027	-45
5	0	1000	0	0	0	11.2	0.051	- 1
5	0	5000	0	0	0	10.2	0.046	-10
5	0	10000	0	0	0	10.2	0.045	-10
5	0	0	50	0	0	11.5	0.052	+ 2
5	0	0	200	0	0	12.0	0.054	+ 6
5	0	0	500	0	0	12.3	0.054	+ 8
5	0	0	0	50	0	11.5	0.051	+ 1
5	0	0	0	200	0	11.9	0.053	+ 5
5	0	0	0	500	0	11.9	0.053	+ 5
5	0	0	0	0	50	11.7	0.053	+ 3
5	0	0	0	0	200	11.7	0.052	+ 3
5	0	0	0	0	500	11.5	0.051	+ 1
5	250	500	0	0	0	6.8	0.031	-40
5	500	5000	0	0	0	6.1	0.027	-47

*0.2% K added; N_2O-C_2H_2 flame

TABLE 9. SECOND INTERFERENCE STUDY FOR THE ANALYSIS OF BARIUM*

ppm Ba	ppm Major Constituents Added						Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	Mg	Mn	PO_4			
5	0	0	0	0	0	0	16.4	0.067	0
5	50	0	0	0	0	0	16.0	0.061	-2
5	100	0	0	0	0	0	15.9	0.064	-3
5	500	0	0	0	0	0	15.5	0.064	-5
5	1000	0	0	0	0	0	15.5	0.064	-5
5	0	0	0	0	0	0	15.4	0.064	0
5	0	50	0	0	0	0	15.6	0.064	+1
5	0	200	0	0	0	0	15.4	0.064	0
5	0	500	0	0	0	0	15.2	0.064	-1
5	0	0	0	0	0	0	15.4	0.064	0
5	0	0	1000	0	0	0	14.9	0.061	-3
5	0	0	5000	0	0	0	14.6	0.061	-5
5	0	0	10000	0	0	0	14.1	0.058	-8
5	0	0	0	0	0	0	15.3	0.064	0
5	0	0	0	50	0	0	15.5	0.064	+1
5	0	0	0	200	0	0	15.0	0.064	-2
5	0	0	0	500	0	0	14.8	0.061	-3
5	0	0	0	0	0	0	14.7	0.061	0
5	0	0	0	0	50	0	14.7	0.061	0
5	0	0	0	0	200	0	14.5	0.058	-1
5	0	0	0	0	500	0	14.5	0.058	-1
5	0	0	0	0	0	0	14.6	0.059	0
5	0	0	0	0	0	50	14.6	0.059	0
5	0	0	0	0	0	200	14.6	0.059	0
5	0	0	0	0	0	500	14.5	0.059	0
5	0	0	0	0	0	0	14.6	0.059	0
5	500	250	5000	250	250	250	14.2	0.059	-3

*0.2% La and 0.2% Na added; N_2O-C_2H_2 flame

TABLE 10. INTERFERENCE STUDY FOR THE ANALYSIS OF BERYLLIUM*

ppm Be	ppm Major Constituents Added				Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Mg	Mn			
1	0	0	0	0	15.7	0.134	0
1	100	0	0	0	14.9	0.127	- 5
1	500	0	0	0	13.0	0.110	-17
1	1000	0	0	0	11.8	0.099	-25
1	0	1000	0	0	16.5	0.142	+ 5
1	0	5000	0	0	16.1	0.138	+ 3
1	0	10000	0	0	16.0	0.136	+ 2
1	0	0	50	0	15.9	0.135	+ 2
1	0	0	200	0	15.9	0.134	+ 2
1	0	0	500	0	16.0	0.138	+ 2
1	0	0	0	50	16.0	0.138	+ 2
1	0	0	0	200	15.8	0.135	+ 1
1	0	0	0	500	15.9	0.136	+ 2
1	500	500	0	0	13.0	0.109	-16
1	500	5000	0	0	13.7	0.115	-13
1	250	5000	0	0	14.2	0.120	- 9

*N_2O-C_2H_2 flame

TABLE 11. THE USE OF OXINE TO CONTROL INTERFERENCES IN THE ANALYSIS OF BERYLLIUM *

ppm Be	ppm Al Added	% Oxine Added	Peak Height (cm)	Net Change (%)
1	0	0	6.1	0
1	0	0.15	6.1	0
1	0	0.25	6.1	0
1	500	0	5.3	-13
1	500	0.10	5.3	-13
1	500	0.20	5.4	-11
1	500	0.40	5.5	-10

*N_2O-C_2H_2 flame

TABLE 12. ALUMINUM, CALCIUM, AND PHOSPHATE INTERFERENCE STUDY FOR THE ANALYSIS OF BERYLLIUM*

	ppm Major Constituents Added				Peak Height		Net Change
ppm Be	Al	Ca	PO_4	La	(cm)	Absorbance	(%)
1	0	0	0	0	19.0	0.171	0
1	500	0	0	0	13.7	0.124	-28
1	0	50	0	0	18.2	0.163	- 4
1	0	200	0	0	18.5	0.166	- 3
1	0	500	0	0	19.0	0.169	0
1	0	0	50	0	19.1	0.170	0
1	0	0	200	0	19.0	0.167	0
1	0	0	500	0	19.3	0.169	+ 2
1	500	0	0	1000	14.1	0.127	-26

*N_2O-C_2H_2 flame

TABLE 13. FIRST INTERFERENCE STUDY FOR THE ANALYSIS OF CALCIUM*

ppm Ca	ppm Major Constituents Added					Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Mg	Mn	PO_4			
5	0	0	0	0	0	13.7	0.251	0
5	50	0	0	0	0	13.5	0.250	-1
5	100	0	0	0	0	13.6	0.250	-1
5	500	0	0	0	0	12.2	0.232	-11
5	1000	0	0	0	0	9.8	0.200	-28
5	0	50	0	0	0	13.5	0.248	-1
5	0	100	0	0	0	13.0	0.238	-5
5	0	500	0	0	0	12.7	0.230	-7
5	0	1000	0	0	0	12.8	0.237	-6
5	0	0	50	0	0	13.4	0.250	-2
5	0	0	100	0	0	13.4	0.248	-2
5	0	0	200	0	0	12.8	0.233	-6
5	0	0	500	0	0	12.9	0.238	-5
5	0	0	0	50	0	13.8	0.256	+1
5	0	0	0	100	0	13.3	0.242	-3
5	0	0	0	200	0	13.0	0.240	-5
5	0	0	0	500	0	11.7	0.214	-14
5	0	0	0	0	10	13.5	0.245	-1
5	0	0	0	0	70	13.4	0.246	-1
5	0	0	0	0	130	13.1	0.242	-4
5	0	0	0	0	200	13.0	0.242	-5
5	0	0	0	0	850	8.6	0.167	-37
5	1000	1000	500	500	200	6.9	0.124	-50

*0.2% La and 0.2% Na added; Air-C_2H_2 flame

TABLE 14. SECOND INTERFERENCE STUDY FOR THE ANALYSIS OF CALCIUM*

ppm Ca	ppm Major Constituent Added					Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Mg	Mn	PO_4			
5	0	0	0	0	0	12.2	0.456	0
5	50	0	0	0	0	10.2	0.378	-16
5	100	0	0	0	0	9.2	0.341	-24
5	500	0	0	0	0	6.7	0.249	-45
5	1000	0	0	0	0	6.9	0.258	-43
5	0	50	0	0	0	12.0	0.443	-1
5	0	100	0	0	0	12.1	0.450	0
5	0	500	0	0	0	11.9	0.445	-2
5	0	1000	0	0	0	11.9	0.441	-2
5	0	0	50	0	0	11.9	0.441	-2
5	0	0	100	0	0	12.1	0.451	0
5	0	0	200	0	0	12.0	0.447	-1
5	0	0	500	0	0	12.0	0.445	-1
5	0	0	0	50	0	12.0	0.445	-1
5	0	0	0	100	0	12.1	0.450	0
5	0	0	0	200	0	12.1	0.450	0
5	0	0	0	500	0	12.0	0.447	-1
5	0	0	0	0	10	12.2	0.450	0
5	0	0	0	0	70	12.2	0.450	0
5	0	0	0	0	130	12.3	0.459	+1
5	0	0	0	0	200	12.0	0.445	-1
5	0	0	0	0	850	12.1	0.446	0
5	1000	1000	500	500	200	7.6	0.250	-37

*0.2% Na added; N_2O-C_2H_2 flame

TABLE 15. THIRD INTERFERENCE STUDY FOR THE ANALYSIS OF CALCIUM*

ppm Ca	ppm Major Constituents Added					Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Mg	Mn	PO_4			
5	0	0	0	0	0	12.0	0.445	0
5	50	0	0	0	0	12.2	0.450	+2
5	100	0	0	0	0	12.4	0.463	+3
5	500	0	0	0	0	11.8	0.442	-2
5	1000	0	0	0	0	10.8	0.402	-10
5	0	50	0	0	0	12.1	0.451	+1
5	0	100	0	0	0	11.7	0.438	-3
5	0	500	0	0	0	11.7	0.430	-3
5	0	1000	0	0	0	12.4	0.462	+3
5	0	0	50	0	0	12.0	0.444	0
5	0	0	100	0	0	11.8	0.444	-2
5	0	0	200	0	0	11.9	0.443	-1
5	0	0	500	0	0	11.9	0.440	-1
5	0	0	0	50	0	12.1	0.450	+1
5	0	0	0	100	0	12.1	0.450	+1
5	0	0	0	200	0	11.7	0.437	-3
5	0	0	0	500	0	11.4	0.424	-5
5	0	0	0	0	10	11.8	0.444	-2
5	0	0	0	0	70	11.7	0.438	-3
5	0	0	0	0	130	12.1	0.462	+1
5	0	0	0	0	200	12.1	0.445	+1
5	0	0	0	0	850	11.6	0.427	-3
5	1000	1000	500	200	200	10.5	0.390	-13

*0.2% La and 0.2% Na added; N_2O-C_2H_2 flame

TABLE 16. COMPARISON OF CALCIUM RESULTS FROM MSA AND AQUEOUS CALIBRATED IN TWO FLAMES, WITH AND WITHOUT LANTHANUM

Sample	Additives	Flame Type	Figure	ppm Ca in Sample		% Deviation between Aqueous and MSA values
				Aqueous	MSA	
GP-7	0.2% Na	Air-C_2H_2	17	2.7	11.9	-77
GP-7	0.2% Na	N_2O-C_2H_2	20	62	122	-49
PA-1	0.2% Na	Air-C_2H_2	18	1.6	5.0	-68
PA-1	0.2% Na	N_2O-C_2H_2	21	1106	1369	-19
GP-2	0.2% Na + 0.2% La	Air-C_2H_2	23	162	163	0
GP-2	0.2% Na + 0.2% La	N_2O-C_2H_2	24	170	178	-4
PA-5	0.2% Na + 0.2% La	Air-C_2H_2	25	283	275	+3
PA-5	0.2% Na + 0.2% La	N_2O-C_2H_2	26	254	262	-4

TABLE 17. FIRST INTERFERENCE STUDY FOR THE ANALYSIS OF CHROMIUM*

ppm Cr	ppm Major Constituents Added							Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	K	Mg	Mn	PO_4			
3	0	0	0	0	0	0	0	11.0	0.049	0
3	100	0	0	0	0	0	0	12.1	0.054	+10
3	500	0	0	0	0	0	0	12.4	0.055	+13
3	1000	0	0	0	0	0	0	12.4	0.055	+13
3	0	0	0	0	0	0	0	11.0	0.049	0
3	0	50	0	0	0	0	0	12.2	0.053	+11
3	0	200	0	0	0	0	0	12.7	0.057	+15
3	0	500	0	0	0	0	0	13.1	0.060	+19
3	0	0	0	0	0	0	0	11.2	0.048	0
3	0	0	100	0	0	0	0	12.1	0.052	+8
3	0	0	1000	0	0	0	0	12.7	0.057	+17
3	0	0	5000	0	0	0	0	12.7	0.057	+17
3	0	0	10000	0	0	0	0	12.4	0.057	+11
3	0	0	0	0	0	0	0	11.1	0.050	0
3	0	0	0	50	0	0	0	12.7	0.057	+14
3	0	0	0	200	0	0	0	13.2	0.062	+19
3	0	0	0	500	0	0	0	13.5	0.062	+22
3	0	0	0	0	0	0	0	11.2	0.052	0
3	0	0	0	0	50	0	0	12.3	0.055	+10
3	0	0	0	0	200	0	0	12.5	0.059	+11
3	0	0	0	0	500	0	0	12.6	0.059	+13
3	0	0	0	0	0	0	0	11.2	0.053	0
3	0	0	0	0	0	50	0	11.8	0.055	+5
3	0	0	0	0	0	200	0	12.1	0.059	+8
3	0	0	0	0	0	500	0	12.5	0.059	+12
3	0	0	0	0	0	0	0	11.3	0.054	0
3	0	0	0	0	0	0	50	12.3	0.059	+9
3	0	0	0	0	0	0	200	13.2	0.062	+17
3	0	0	0	0	0	0	500	13.7	0.064	+21
3	0	0	0	0	0	0	0	11.2	0.054	0
3	250	2500	25	25	25	25	25	11.4	0.054	+2

*N_2O-C_2H_2 flame

TABLE 18. SECOND INTERFERENCE STUDY FOR THE ANALYSIS OF CHROMIUM*

ppm Cr	ppm Major Constituents Added						Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	Mg	Mn	PO_4			
3	0	0	0	0	0	0	13.5	0.067	0
3	100	0	0	0	0	0	13.5	0.066	0
3	500	0	0	0	0	0	13.5	0.066	0
3	1000	0	0	0	0	0	13.4	0.066	-1
3	0	0	0	0	0	0	13.4	0.066	0
3	0	50	0	0	0	0	13.5	0.066	+1
3	0	200	0	0	0	0	13.7	0.067	+2
3	0	500	0	0	0	0	13.6	0.067	+1
3	0	0	0	0	0	0	13.5	0.062	0
3	0	0	100	0	0	0	13.6	0.061	+1
3	0	0	1000	0	0	0	13.4	0.060	-1
3	0	0	5000	0	0	0	12.7	0.058	-6
3	0	0	10000	0	0	0	12.1	0.056	-11
3	0	0	0	0	0	0	13.9	0.070	0
3	0	0	0	50	0	0	13.8	0.070	-1
3	0	0	0	200	0	0	13.5	0.061	-3
3	0	0	0	500	0	0	13.5	0.061	-3
3	0	0	0	0	0	0	13.2	0.061	0
3	0	0	0	0	50	0	13.3	0.061	0
3	0	0	0	0	200	0	13.3	0.061	+2
3	0	0	0	0	500	0	13.4	0.064	+2
3	0	0	0	0	0	0	13.5	0.064	0
3	0	0	0	0	0	50	13.5	0.064	0
3	0	0	0	0	0	200	13.5	0.064	0
3	0	0	0	0	0	500	13.8	0.067	+2
3	0	0	0	0	0		13.5	0.064	0
3	250	25	2500	25	25	25	13.8	0.061	-2

*0.2% Na added; N_2O-C_2H_2 flame

TABLE 19. INTERFERENCE STUDY FOR THE ANALYSIS OF COBALT*

ppm Co	ppm Major Constituents Added					Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	K	Mg	Mn			
2	0	0	0	0	0	6.4	0.055	0
2	100	0	0	0	0	6.2	0.054	-3
2	500	0	0	0	0	6.3	0.054	-2
2	1000	0	0	0	0	6.3	0.054	-2
2	0	1000	0	0	0	6.2	0.053	-3
2	0	5000	0	0	0	6.3	0.054	-2
2	0	10000	0	0	0	6.1	0.053	-5
2	0	0	50	0	0	6.6	0.056	+3
2	0	0	200	0	0	6.5	0.057	+2
2	0	0	500	0	0	6.5	0.057	+2
2	0	0	0	50	0	6.2	0.053	-3
2	0	0	0	200	0	6.3	0.053	-2
2	0	0	0	500	0	6.3	0.055	-2
2	0	0	0	0	50	6.3	0.055	-2
2	0	0	0	0	200	6.4	0.055	0
2	0	0	0	0	500	6.4	0.055	0

*Air-C_2H_2 flame

TABLE 20. CALCIUM AND PHOSPHATE INTERFERENCE STUDY FOR THE ANALYSIS OF COBALT*

ppm Co	ppm Major Constituents Added		Peak Height (cm)	Absorbance	Net Change (%)
	Ca	PO_4			
2	0	0	6.3	0.053	0
2	50	0	6.3	0.053	0
2	200	0	6.3	0.053	0
2	500	0	6.4	0.053	+2
2	0	50	6.5	0.054	+3
2	0	200	6.5	0.054	+3
2	0	500	6.5	0.054	+3
2	500	500	6.5	0.054	+3

*Air-C_2H_2 flame

TABLE 21. INTERFERENCE STUDY FOR COPPER ANALYSIS

ppm Cu	Added Constituents		Apparent Concentration of Cu (ppm)	% Net Change
	ppm Fe	ppm Al		
3.00	0	0	3.00	0
3.00	200	0	3.07	+2.4
3.00	0	500	2.85	-4.9
3.00	200	200	3.02	+0.8
3.00	200	500	3.02	+0.8

TABLE 22. INTERFERENCE STUDY FOR THE ANALYSIS OF LEAD*

ppb Pb	ppm Metal Added							Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	K	Mg	Mn	PO_4			
5	0	0	0	0	0	0	0	16.0	0.022	0
5	100	0	0	0	0	0	0	16.1	0.022	+1
5	500	0	0	0	0	0	0	16.1	0.022	+1
5	1000	0	0	0	0	0	0	15.9	0.021	-1
5	0	50	0	0	0	0	0	16.6	0.023	+4
5	0	200	0	0	0	0	0	16.7	0.023	+5
5	0	500	0	0	0	0	0	16.7	0.023	+5
5	0	0	100	0	0	0	0	16.3	0.022	+2
5	0	0	500	0	0	0	0	16.1	0.022	+1
5	0	0	1000	0	0	0	0	16.2	0.022	+1
5	0	0	5000	0	0	0	0	15.9	0.022	-1
5	0	0	10000	0	0	0	0	15.6	0.022	-2
5	0	0	0	50	0	0	0	16.5	0.023	+3
5	0	0	0	200	0	0	0	16.4	0.023	+2
5	0	0	0	500	0	0	0	16.4	0.023	+2
5	0	0	0	0	50	0	0	16.4	0.023	+2
5	0	0	0	0	200	0	0	16.6	0.023	+4
5	0	0	0	0	500	0	0	16.6	0.023	+4
5	0	0	0	0	0	50	0	16.6	0.022	+4
5	0	0	0	0	0	200	0	16.6	0.022	+4
5	0	0	0	0	0	500	0	16.7	0.022	+4
5	0	0	0	0	0	0	50	16.6	0.023	+4
5	0	0	0	0	0	0	200	17.0	0.023	+6
5	0	0	0	0	0	0	500	16.8	0.023	+5
5	0	0	0	0	0	0	1000	17.0	0.023	+6
5	1000	500	10000	500	500	500	500	15.6	0.021	-3

*Air-C_2H_2 flame

TABLE 23. INTERFERENCE STUDY FOR THE ANALYSIS OF SELENIUM*

ppm Se	ppm Metal Added					Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Ca	K	Mg			
5	0	0	0	0	0	14.7	0.098	0
5	25	0	0	0	0	0.5	0.000	-96
5	50	0	0	0	0	0.6	0.001	-96
5	100	0	0	0	0	0.8	0.001	-95
5	500	0	0	0	0	1.7	0.005	-88
5	1000	0	0	0	0	1.2	0.004	-92
5	0	50	0	0	0	7.4	0.047	-50
5	0	100	0	0	0	6.3	0.040	-57
5	0	500	0	0	0	4.2	0.020	-72
5	0	1000	0	0	0	3.6	0.023	-76
5	0	0	50	0	0	5.6	0.034	-62
5	0	0	100	0	0	5.2	0.033	-65
5	0	0	200	0	0	5.7	0.033	-61
5	0	0	500	0	0	5.1	0.033	-65
5	0	0	0	50	0	13.7	0.091	-7
5	0	0	0	100	0	14.1	0.096	-4
5	0	0	0	200	0	14.6	0.098	-1
5	0	0	0	500	0	14.1	0.094	-4
5	0	0	0	0	50	5.6	0.035	-62
5	0	0	0	0	100	5.6	0.035	-65
5	0	0	0	0	200	5.1	0.032	-65
5	0	0	0	0	500	4.8	0.030	-67

*Ar-H_2 flame

TABLE 24. USE OF ADDITIVES TO CONTROL INTERFERENCES IN THE ANALYSIS OF SELENIUM*

ppm Se	ppm Al	ppm Additive				Peak Height (cm)	Absorbance	Net Change (%)
		EDTA	La	Na	Na_2-EDTA			
5	0	0	0	0	0	8.8	0.113	0
5	100	0	0	0	0	1.1	0.007	-88
5	0	0	0	2000	0	7.7	0.099	-13
5	50	0	0	2000	0	5.9	0.076	-33
5	0	0	1000	0	0	1.3	0.015	-85
5	100	0	100	0	0	2.2	0.027	-75
5	0	2000	0	0	0	8.7	0.112	-1
5	100	2000	0	0	0	1.9	0.245	-78
5	0	0	0	0	2000	4.7	0.061	-46

*Ar-H_2 flame

TABLE 25. COMPARISON OF RESULTS OF SELENIUM ANALYSIS BY THREE AAS FLAME METHODS

Sample	ppm Selenium		
	Ar-H_2 flame	Air-C_2H_2 Flame	N_2O-C_2H_2 Flame
GP-10-SP*	20	66	55
GP-12-SP*	14	64	55
GP-20-SP*	17	82	55

*Sample spiked with 50 ppm selenium on a dry weight basis.

TABLE 26. FIRST INTERFERENCE STUDY FOR THE ANALYSIS OF STRONTIUM*

ppm Sr	ppm Major Constituents Added				Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Mn	PO_4			
4	0	0	0	0	19.4	0.248	0
4	100	0	0	0	17.2	0.238	-11
4	500	0	0	0	14.6	0.194	-25
4	1000	0	0	0	13.5	0.180	-30
4	0	0	0	0	19.4	0.248	0
4	0	500	0	0	19.2	0.250	-1
4	0	1000	0	0	19.4	0.251	0
4	0	9000	0	0	18.6	0.245	-4
4	0	0	0	0	19.5	0.252	0
4	0	0	50	0	19.7	0.260	+1
4	0	0	200	0	19.7	0.260	+1
4	0	0	500	0	19.8	0.260	+1
4	0	0	0	0	19.5	0.252	0
4	0	0	0	50	19.8	0.260	+2
4	0	0	0	200	19.8	0.260	+2
4	0	0	0	500	19.8	0.260	+2

*0.2% K added; N_2O-C_2H_2 flame

TABLE 27. SECOND INTERFERENCE STUDY FOR THE ANALYSIS OF STRONTIUM*

ppm Sr	ppm Major Constituents Added				Peak Height (cm)	Absorbance	Net Change (%)
	Al	Fe	Mn	PO_4			
4	0	0	0	0	19.4	0.260	0
4	100	0	0	0	20.2	0.270	+4
4	500	0	0	0	20.2	0.270	+4
4	1000	0	0	0	19.6	0.255	+1
4	0	0	0	0	19.5	0.260	0
4	0	500	0	0	19.2	0.255	-2
4	0	1000	0	0	19.4	0.255	0
4	0	9000	0	0	18.4	0.241	-5
4	0	0	0	0	19.4	0.260	0
4	0	0	50	0	20.0	0.266	+3
4	0	0	200	0	20.0	0.266	+3
4	0	0	500	0	19.8	0.266	+2
4	0	0	0	0	19.1	0.260	0
4	0	0	0	50	19.3	0.267	+1
4	0	0	0	200	17.6	0.237	-8
4	0	0	0	500	16.0	0.220	-16

*1.0% La and 0.2% K added; N_2O-C_2H_2 flame

TABLE 28. THIRD INTERFERENCE STUDY FOR THE ANALYSIS OF STRONTIUM*

ppm Sr	ppm Major Constituents Added						Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	Mg	Mn	PO_4			
2	0	0	0	0	0	0	18.2	0.078	0
2	10	0	0	0	0	0	17.1	0.074	-6
2	30	0	0	0	0	0	17.5	0.075	-4
2	50	0	0	0	0	0	17.4	0.076	-4
2	70	0	0	0	0	0	17.4	0.076	-4
2	100	0	0	0	0	0	17.5	0.076	-4
2	500	0	0	0	0	0	16.9	0.073	-7
2	1000	0	0	0	0	0	16.0	0.070	-12
2	0	50	0	0	0	0	17.7	0.071	-3
2	0	200	0	0	0	0	17.3	0.073	-4
2	0	500	0	0	0	0	17.3	0.073	-4
2	0	0	500	0	0	0	17.0	0.072	-6
2	0	0	1000	0	0	0	16.6	0.071	-8
2	0	0	5000	0	0	0	14.7	0.062	-19
2	0	0	10000	0	0	0	12.6	0.052	-31
2	0	0	0	50	0	0	16.8	0.072	-8
2	0	0	0	200	0	0	16.2	0.071	-11
2	0	0	0	500	0	0	16.0	0.070	-11
2	0	0	0	0	50	0	16.9	0.072	-7
2	0	0	0	0	200	0	17.4	0.078	-3
2	0	0	0	0	500	0	17.0	0.077	-7
2	0	0	0	0	0	50	17.1	0.076	-6
2	0	0	0	0	0	200	17.7	0.079	-3
2	0	0	0	0	0	500	16.0	0.070	-11

*1% La and 0.2% K added; air-C_2H_2 flame

TABLE 29. THE COMPARISON OF STRONTIUM ANALYSES USING VARIOUS METHODS

Sample	Flame	Additives	Figure	ppm Sr in Sample		% Deviation between Aqueous and MSA values
				Aqueous	MSA	
PA-14-SP	Air-C_2H_2	0.2% Na + 1 % La	42	38	68	-44
PA-14-SP	N_2O-C_2H_2	0.2% Na	40	47	65	-28
PA-14-SP	N_2O-C_2H_2	0.2% Na + 1% La	41	60	60	0
PA-15	Air-C_2H_2	0.2% Na + 1% La	42	10	14	-29
PA-15	N_2O-C_2H_2	0.2% Na	40	9.4	14	-33
PA-15	N_2O-C_2H_2	0.2% Na + 1% La	41	12	13	-8

TABLE 30. FIRST INTERFERENCE STUDY FOR THE ANALYSIS OF TITANIUM*

ppm Ti	ppm Major Constituents Added				Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	PO_4			
30	0	0	0	0	12.2	0.084	0
30	20	0	0	0	13.0	0.089	+7
30	60	0	0	0	13.4	0.091	+10
30	100	0	0	0	13.3	0.090	+9
30	500	0	0	0	13.0	0.089	+7
30	1000	0	0	0	12.5	0.086	+3
30	2000	0	0	0	12.1	0.082	-1
30	0	0	0	0	12.1	0.083	0
30	0	50	0	0	11.3	0.077	-7
30	0	200	0	0	11.3	0.078	-7
30	0	500	0	0	11.8	0.076	-3
30	0	0	0	0	12.0	0.082	0
30	0	0	100	0	11.6	0.080	-3
30	0	0	500	0	11.2	0.076	-6
30	0	0	1000	0	11.1	0.076	-4
30	0	0	5000	0	10.9	0.076	-9
30	0	0	10000	0	10.0	0.069	-17
30	0	0	0	0	11.4	0.075	0
30	0	0	0	50	11.2	0.075	-2
30	0	0	0	200	11.6	0.075	+2
30	0	0	0	500	10.9	0.076	-4
30	0	0	0	0	11.4	0.075	0
30	500	50	5000	0	12.2	0.083	+7

*0.2% Na added; N_2O-C_2H_2 flame

TABLE 31. SECOND INTERFERENCE STUDY FOR THE ANALYSIS OF TITANIUM*

ppm Ti	ppm Major Constituents Added			Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe			
30	0	0	0	16.1	0.113	0
30	100	0	0	5.7	0.040	-65
30	500	0	0	6.0	0.044	-63
30	1000	0	0	5.6	0.040	-65
30	0	0	0	16.1	0.113	0
30	0	50	0	17.5	0.122	+9
30	0	200	0	17.5	0.122	+9
30	0	500	0	17.5	0.122	+9
30	0	0	0	16.1	0.113	0
30	0	0	1000	14.4	0.099	-11
30	0	0	5000	13.2	0.093	-18
30	0	0	9000	13.3	0.093	-18
30	0	0	0	16.1	0.113	0
30	430	0	325	6.4	0.046	-60

*1% La and 0.2% Na added; N_2O-C_2H_2 flame

TABLE 32. FIRST INTERFERENCE STUDY FOR THE ANALYSIS OF VANADIUM*

ppm V	ppm Major Constituents Added							Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	K	Mg	Mn	PO_4			
6	0	0	0	0	0	0	0	5.8	0.015	0
6	20	0	0	0	0	0	0	7.0	0.019	+21
6	60	0	0	0	0	0	0	7.0	0.019	+21
6	100	0	0	0	0	0	0	7.6	0.019	+31
6	500	0	0	0	0	0	0	7.6	0.019	+31
6	1000	0	0	0	0	0	0	7.6	0.019	+31
6	2000	0	0	0	0	0	0	7.4	0.019	+29
6	0	0	0	0	0	0	0	5.5	0.015	0
6	0	50	0	0	0	0	0	6.1	0.017	+11
6	0	200	0	0	0	0	0	7.3	0.020	+33
6	0	500	0	0	0	0	0	7.5	0.021	+36
6	0	0	0	0	0	0	0	5.6	0.015	0
6	0	0	500	0	0	0	0	5.1	0.013	-9
6	0	0	1000	0	0	0	0	4.9	0.012	-13
6	0	0	5000	0	0	0	0	4.5	0.010	-20
6	0	0	10000	0	0	0	0	4.1	0.009	-27
6	0	0	0	0	0	0	0	5.5	0.015	0
6	0	0	0	50	0	0	0	6.8	0.019	+24
6	0	0	0	200	0	0	0	7.2	0.020	+31
6	0	0	0	500	0	0	0	7.5	0.021	+36
6	0	0	0	0	0	0	0	5.6	0.015	0
6	0	0	0	0	50	0	0	6.7	0.019	+20
6	0	0	0	0	200	0	0	6.8	0.019	+21
6	0	0	0	0	500	0	0	6.8	0.019	+21
6	0	0	0	0	0	0	0	5.6	0.015	0
6	0	0	0	0	0	50	0	5.7	0.015	+2
6	0	0	0	0	0	200	0	6.0	0.016	+7
6	0	0	0	0		500	0	6.5	0.018	+16

*N_2O-C_2H_2 flame

(continued)

TABLE 32 (continued)

ppm V	ppm Major Constituents Added							Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	K	Mg	Mn	PO_4			
6	0	0	0	0	0	0	0	5.5	0.015	0
6	0	0	0	0	0	0	50	6.5	0.018	+18
6	0	0	0	0	0	0	200	7.2	0.020	+31
6	0	0	0	0	0	0	500	7.2	0.020	+31

TABLE 33. SECOND INTERFERENCE STUDY FOR THE ANALYSIS OF VANADIUM*

ppm V	ppm Major Constituents Added						Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	Mg	Mn	PO_4			
6	0	0	0	0	0	0	8.2	0.022	0
6	20	0	0	0	0	0	8.4	0.022	+2
6	60	0	0	0	0	0	8.5	0.023	+4
6	100	0	0	0	0	0	8.4	0.022	+2
6	500	0	0	0	0	0	8.5	0.022	+4
6	1000	0	0	0	0	0	8.4	0.022	+2
6	2000	0	0	0	0	0	8.2	0.022	0
6	0	0	0	0	0	0	8.1	0.021	0
6	0	50	0	0	0	0	8.0	0.020	-1
6	0	200	0	0	0	0	8.2	0.022	+1
6	0	500	0	0	0	0	8.5	0.022	+5
6	0	0	0	0	0	0	8.1	0.021	0
6	0	0	100	0	0	0	7.8	0.018	-4
6	0	0	500	0	0	0	7.4	0.018	-9
6	0	0	1000	0	0	0	7.3	0.018	-10
6	0	0	5000	0	0	0	6.7	0.018	-17
6	0	0	1000	0	0	0	6.5	0.017	-20
6	0	0	0	0	0	0	7.9	0.020	0
6	0	0	0	50	0	0	8.0	0.020	+1
6	0	0	0	200	0	0	7.8	0.020	-1
6	0	0	0	500	0	0	7.9	0.020	0
6	0	0	0	0	0	0	7.9	0.020	0
6	0	0	0	0	50	0	7.8	0.020	-1
6	0	0	0	0	200	0	7.8	0.020	-1
6	0	0	0	0	500	0	7.9	0.020	0
6	0	0	0	0	0	0	7.9	0.020	0
6	0	0	0	0	0	50	7.9	0.020	0
6	0	0	0	0	0	200	7.9	0.020	0
6	0	0	0	0	0	500	7.9	0.020	0

*0.2% Na added; N_2O-C_2H_2 flame

(continued)

TABLE 33 (continued)

ppm V	ppm Major Constituents Added						Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe	Mg	Mn	PO_4			
6	0	0	0	0	0	0	7.8	0.020	0
6	500	50	1000	50	50	50	8.1	0.020	+4
6	500	50	5000	50	50	50	8.1	0.020	+4

TABLE 34. THIRD INTERFERENCE STUDY FOR THE ANALYSIS OF VANADIUM*

ppm V	ppm Major Constituents Added			Peak Height (cm)	Absorbance	Net Change (%)
	Al	Ca	Fe			
6	0	0	0	15.3	0.026	0
6	100	0	0	15.4	0.026	0
6	500	0	0	15.3	0.026	0
6	1000	0	0	15.3	0.026	0
6	0	0	0	15.5	0.026	0
6	0	50	0	15.5	0.027	0
6	0	200	0	15.7	0.027	+3
6	0	500	0	15.7	0.027	+3
6	0	0	0	15.3	0.026	0
6	0	0	100	15.2	0.025	-1
6	0	0	5000	15.1	0.025	-1
6	0	0	9000	15.4	0.025	+1

*1% La and 0.2% Na added; N_2O-C_2H_2 flame.

TABLE 35. THE ANALYSIS OF VANADIUM IN PA-17

Flame Type	Figure #	Additives	ppm V in PA-17	
			Aqueous	MSA
N_2O-C_2H_2	46	0.2% Na	25	24
N_2O-C_2H_2	47	0.2% Na + 1% La	24	23

TABLE 36. CONDITIONS USED FOR THE FINAL ANALYSIS OF SOIL (GP) AND SEDIMENT (PA) SAMPLES

Element	Wavelength (nm)	Spectral Band Width (nm)	Flame Type	Interferences	Corrective Measures	Detection Limit (ppm)
Ba	553.6	0.4	N_2O-C_2H_2	Ionization effect	Addition of 0.2% potassium or sodium to all solutions	6
				Al, Fe	Addition of 0.2% of lanthanum to all solutions	
Be	234.9	0.7	N_2O-C_2H_2	Al	Use of matrix-matched standards Addition of oxine	0.4
Ca	422.7	1.4	N_2O-C_2H_2	Ionization effect	Addition of 0.2% potassium or sodium to all solutions	2
				Al	Addition of 0.2% lanthanum and sodium to all solutions	
Co	240.7	0.2	Air-C_2H_2	None	No corrective measures required	3.0
Cr	357.9	0.7	N_2O-C_2H_2	Ionization effect	Addition of 0.2% potassium or sodium to all solutions	
				Fe	Use of matrix-matched standards for samples containing >500 ppm Fe	2
Cu	324.8	0.7	Air-C_2H_2	None	No corrective measures required	0.6
Mn	279.5	0.2	Air-C_2H_2	None	No corrective measures required	0.5

TABLE 36. (Continued)

Element	Wavelength (nm)	Spectral Band Width (nm)	Flame Type	Interferences	Corrective Measures	Detection Limit (ppm)
Ni	232.0	0.2	Air-C_2H_2	None	No corrective measures required	2
Pb	283.3	0.7	Air-C_2H_2	None	No corrective measures required	4.0
Se	196.0	0.7	N_2O-C_2H_2	To be defined	To be defined	25
Sr	460.7	1.4	N_2O-C_2H_2	Ionization effect	Addition of 0.2% potassium or sodium to all solutions	1.5
				Al	Addition of 0.2% lanthanum to all solutions	
Ti	365.3	0.2	N_2O-C_2H_2	Ionization effect	Addition of 0.2% potassium to all solutions	25
				Fe	Use of matrix-matched standards for samples containing >5000 ppm Fe	
V	318.4	0.7	N_2O-C_2H_2	Ionization effect	Addition of 0.2% potassium or sodium to all solutions	6.0
				Fe	Addition of 0.2% lanthanum to all solutions	
Zn	213.9	0.7	Air-C_2H_2	None	No corrective measures required	0.7

TABLE 37. CALCIUM CONCENTRATIONS IN SOIL (GP) SAMPLES AND SEDIMENT (PA) SAMPLES*

Sample	ppm Ca	Sample	ppm Ca
GP-1	90.7	PA-1	933
GP-2	177	PA-2	273
GP-3	180	PA-3	341
GP-4	386	PA-4	1780
GP-5	204	PA-5	205
GP-6	111	PA-6	1590
GP-7	97.0	PA-7	246
GP-8	89.5	PA-8	147
GP-9	48.3	PA-9	247
GP-10	206	PA-10	1650
GP-11	45.9	PA-11	280
GP-12	38.6	PA-12	15400
GP-13	584	PA-13	322
GP-14	70.3	PA-14	129
GP-15	37.4	PA-15	252
GP-16	70.1	PA-16	28.4
GP-17	75.1	PA-17	239
GP-18	135		
GP-19	408		
GP-20	78.9		

* 0.2% Na and 0.2% La added; N_2O - C_2H_2 flame.

TABLE 38. FINAL ANALYSIS OF TRACE ELEMENTS IN SOIL (GP) SAMPLES

Sample	ppm Constituent								
	Be	Co	Cr	Cu	Ni	Pb	Ti		Zn
							Aqueous	MM	
GP-1	<0.4	<3.0	5.2	0.8	3.0	8.9	101	87	6.7
GP-2	<0.4	<3.0	5.5	1.7	3.0	8.9	98	84	8.6
GP-3	<0.4	<3.0	3.8	1.2	2.5	9.4	77	66	7.9
GP-4	<0.4	<3.0	4.5	1.7	3.8	8.9	50	43	19.3
GP-5	<0.4	<3.0	6.9	2.1	3.8	8.9	169	145	7.3
GP-6	<0.4	<3.0	4.8	1.7	3.4	7.1	133	115	7.2
GP-7	<0.4	<3.0	5.2	1.7	3.6	8.9	163	141	10.6
GP-8	<0.4	<3.0	5.9	1.7	3.8	8.9	169	145	8.3
GP-9	<0.4	<3.0	8.6	1.7	3.8	9.8	100	94	7.8
GP-10	<0.4	<3.0	21.3	4.1	6.8	8.9	158	136	10.9
GP-11	<0.4	<3.0	6.8	1.7	4.5	7.1	148	128	4.7
GP-12	<0.4	<3.0	4.8	0.8	2.7	<4.0	56	48	3.1
GP-13	<0.4	<3.0	8.6	2.5	4.5	<4.0	44	38	11.6
GP-14	<0.4	<3.0	4.1	1.2	3.0	8.9	80	69	5.0
GP-15	<0.4	<3.0	3.8	0.8	<2.0	4.5	124	107	4.3
GP-16	<0.4	<3.0	2.4	1.2	2.3	6.2	50	43	5.2
GP-17	<0.4	<3.0	5.3	1.2	2.5	8.9	89	77	7.8
GP-18	<0.4	<3.0	5.5	0.8	4.9	7.1	33	28	4.2
GP-19	<0.4	<3.0	5.2	1.7	3.4	11.6	33	28	8.4
GP-20	<0.4	3.0	12.4	2.7	3.8	8.9	62	54	6.4

TABLE 39. FINAL ANALYSIS OF TRACE ELEMENTS IN SEDIMENT (PA) SAMPLES

Sample	ppm Constituent										
	Ba	Be	Co	Cr	Cu	Mn	Ni	Pb	Sr	V	Zn
PA-1	43	0.8	7.5	8.8	12.0	693	16.4	31.2	7.9	12	90
PA-2	47	1.5	19.5	10.3	12.0	2010	30.2	17.9	8.6	13	127
PA-3	43	1.4	11.8	8.8	9.8	985	29.3	21.4	5.7	12	122
PA-4	50	1.4	10.6	12.2	28.5	500	25.8	28.6	19.7	13	121
PA-5	33	1.9	16.5	11.7	12.0	1260	36.7	14.3	5.0	15	156
PA-6	49	1.2	12.2	12.9	62.6	806	25.1	33.0	19.2	14	102
PA-7	26	1.5	13.4	9.8	13.2	701	28.0	17.0	7.9	9.5	121
PA-8	36	1.5	14.4	9.3	10.8	1060	30.4	13.4	7.1	11	124
PA-9	53	1.5	17.3	12.9	16.5	1280	30.2	17.0	10.2	12	133
PA-10	41	1.0	12.2	13.6	12.4	922	23.6	19.6	8.7	14	112
PA-11	39	1.0	13.8	7.8	10.0	1570	31.6	15.2	10.0	9.0	135
PA-12	134	1.4	13.8	31.1	27.3	532	31.6	28.6	31.5	24	116
PA-13	39	1.5	13.4	19.0	20.7	657	26.2	19.6	23.6	20	112
PA-14	51	1.0	15.4	9.4	18.1	504	26.2	21.4	7.9	11	60
PA-15	74	2.2	16.9	27.5	27.3	1300	33.1	21.4	11.6	27	154
PA-16	33	1.9	12.6	21.0	24.1	693	27.3	16.1	15.0	19	118
PA-17	33	1.9	13.8	22.1	26.1	693	28.7	18.7	13.4	22	118

TABLE 40. AAS ANALYSIS OF ELEMENTS IN SHIPPING BLANKS

Shipping Blank	µg Element Present												
	Al	Ag	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K
GP	<20	<5	<300	*	<0.2	<25	77	<1	<13	8	<2	26	8
PA-a	<20	<5	*	<25	<0.2	*	175	<1	<13	33	<2	223	10
PA-b	76	<5	*	<25	<0.2	*	100	<1	<13	8	<2	75	13

TABLE 40 (continued)

Shipping Blank	µg Element Present												
	Mg	Mn	Mo	Na	Ni	Pb	Sb	Se	Sn	Sr	Ti	V	Zn
GP	7	*	*	7	<25	<15	<100	130	<100	*	<50	*	12
PA-a	7	6	<25	50	<25	<15	*	*	*	<5	*	<25	17
PA-b	6	4	<25	50	<25	<15	*	*	*	<5	*	<25	15

* Analysis not required.

TABLE 41. AVERAGES AND STANDARD DEVIATIONS OF DUPLICATE SOIL (GP) AND SEDIMENT (PA) SAMPLES

Sample	Set	Average ppm Trace Constituent and Standard Deviation					
		Ba	Be	Co	Cr	Cu	Mn
GP-3	III	*	†	†	3.8 ± 0.0	1.2 ± 0.0	*
GP-7	III	*	†	†	5.2 ± 0.0	1.7 ± 0.0	*
GP-17	III	*	†	†	5.3 ± 0.2	1.2 ± 0.0	*
PA-2	IV	47 ± 3	1.6 ± 0.0	19.5 ± 0.2	10.7 ± 0.5	12.0 ± 0.0	2010 ± 21
PA-3	IV	43 ± 5	1.4 ± 0.1	11.8 ± 0.8	8.9 ± 0.0	9.8 ± 1.0	985 ± 156
PA-8	IV	36 ± 2	1.6 ± 0.0	14.4 ± 0.6	9.5 ± 0.5	10.8 ± 0.0	1060 ± 220
PA-13	IV	39 ± 1	1.6 ± 0.0	13.4 ± 0.0	19.6 ± 0.2	20.7 ± 0.2	657 ± 12

-continued-

*Analysis not required.

†Average and standard deviation not applicable since element not detectable in sample.

TABLE 41 (continued)

Sample	Set	Average ppm Trace Constituent and Standard Deviation						
		Ni	Pb	Sr	Ti(Aq)	Ti(MM)	V	Zn
GP-3	III	2.5 ± 0.2	9.4 ± 0.4	*	77 ± 6	66 ± 5	*	7.9 ± 0.2
GP-7	III	3.6 ± 0.2	8.9 ± 0.0	*	163 ± 15	141 ± 13	*	10.6 ± 1.1
GP-17	III	2.5 ± 0.2	8.9 ± 0.0	*	89 ± 9	77 ± 7	*	7.8 ± 2.9
PA-2	IV	30.2 ± 0.0	17.9 ± 0.0	8.6 ± 0.2	*	*	13 ± 1	127 ± 6
PA-3	IV	29.3 ± 0.5	21.4 ± 0.0	5.7 ± 0.6	*	*	12 ± 1	122 ± 10
PA-8	IV	30.4 ± 0.2	13.4 ± 0.0	7.1 ± 0.8	*	*	11 ± 1	124 ± 1
PA-13	IV	26.2 ± 0.0	19.6 ± 0.0	23.6 ± 3.4	*	*	20 ± 0	112 ± 0

*Analysis not required.

TABLE 42. PERCENT RECOVERY OF SPIKED SOIL (GP) AND SEDIMENT (PA) SAMPLES

Sample	Set	Recovery					
		Ba	Be	Co	Cr	Cu	Mn
GP-4	III	*	†	#	100	84	*
GP-8	III	*	†	#	101	80	*
GP-19	III	*	†	#	105	88	*
PA-9	IV	61	96	88	94	89	†
PA-14	IV	44	95	88	101	88	†
PA-12	IV	96	87	84	99	90	†

TABLE 42 (continued).

Sample	Set	% Recovery						
		Ni	Pb	Sr	Ti(Aq)	Ti(MM)	V	Zn
GP-4	III	102	74	*	107	92	*	87
GP-8	III	102	75	*	†	†	*	95
GP-19	III	109	89	*	86	74	*	100
PA-9	IV	94	94	90	*	*	86	114
PA-14	IV	95	90	98	*	*	90	†
PA-17	IV	91	84	94	*	*	104	130

*Analysis not required.

†Spike omitted

#Percent recovery not applicable since element not detectable in sample.

TABLE 43. TRACE ELEMENT CONCENTRATIONS IN REFERENCE SEDIMENT B

Reference Sediment	Set	ppm Trace Constituent						
		Ba	Be	Cd	Co	Cr	Cu	Mn
B	II	12	<0.4	*	<3.0	59.7	8.9	8.3
B	II	13	<0.4	*	<3.0	63.3	8.9	7.2
B	III	*	<0.4	0.9	<3.0	49.8	8.3	*
B	IV	14	<0.4	1.0	<3.0	48.4	8.0	6.0
B	IV	14	0.4	1.0	<3.0	50.5	8.8	6.5

TABLE 43 (continued)

Reference Sediment	Set	ppm Trace Constituent					
		Ni	Pb	Sr	Ti	V	Zn
B	II	2.3	8.7	2.3	87	9.2	12.4
B	II	2.3	7.9	2.3	82	10	13.0
B	III	2.3	8.2	*	41	*	12.1
B	IV	2.4	8.0	2.0	*	8.6	11.9
B	IV	2.4	8.0	2.0	*	8.6	13.5

*Analysis not required.

TABLE 44. TRACE ELEMENT CONCENTRATIONS IN REFERENCE SEDIMENT C

Reference Sediment	Set	ppm Trace Constituent						
		Ba	Be	Cd	Co	Cr	Cu	Mn
C	II	26	<0.4	*	<3.0	297	24.5	11.6
C	II	20	<0.4	*	<3.0	320	26.8	15.6
C	II	20	<0.4	*	<3.0	295	24.7	11.4
C	II	20	<0.4	*	<3.0	286	24.2	13.2
C	III	*	<0.4	4.3	<3.0	241	23.8	*
C	III	*	<0.4	4.4	<3.0	245	23.8	*
C	IV	21	<0.4	5.0	<3.0	276	24.1	14.0
C	IV	21	<0.4	4.9	<3.0	268	24.1	12.0

TABLE 44 (continued).

Reference Sediment	Set	ppm Trace Constituent					
		Ni	Pb	Sr	Ti	V	Zn
C	II	2.4	18.0	5.3	70	12	28.0
C	II	2.4	19.0	5.3	122	12	37.4
C	II	2.4	18.0	4.6	46	12	52.0
C	II	2.4	18.0	4.6	82	13	37.0
C	III	2.5	17.0	*	65	*	37.0
C	III	2.5	16.9	*	15	*	38.4
C	III	2.7	16.9	*	71	*	41.0
C	IV	2.4	18.0	5.3	*	10	38.6
C	IV	2.4	18.0	4.2	*	9.2	33.2

*Analysis not required.

TABLE 45. PERCENT RECOVERY OF SPIKED SAMPLES FOR REFERENCE SEDIMENT B

Sample	Set	% Recovery						
		Ba	Be	Cd	Co	Cr	Cu	Mn
B	II	*	94	*	†	95	83	*
B	III	*	102	97	†	97	87	*
B	IV	76	104	94	†	105	95	106

TABLE 45 (continued)

Reference Sediment	Set	% Recovery					
		Ni	Pb	Sr	Ti	V	Zn
B	II	87	93	81	#	117	60
B	III	107	89	*	#	†	100
B	IV	95	94	100	*	97	92

*Analysis not required.

†Percent recovery not applicable since element not detectable in sample.

#Spike omitted.

TABLE 46. PERCENT RECOVERY OF SPIKED SAMPLES FOR REFERENCE SEDIMENT C

Reference Sediment	Set	% Recovery						
		Ba	Be	Cd	Co	Cr	Cu	Mn
C	II	*	83	*	*	#	91	*
C	II	*	85	*	*	104	90	*
C	III	*	97	87	†	94	91	*
C	III	80	101	93	†	112	97	100

TABLE 46 (continued).

Reference Sediment	Set	% Recovery					
		Ni	Pb	Sr	Ti	V	Zn
C	II	86	94	72	#	118	90
C	II	86	94	79	#	118	101
C	III	82	83	*	#	*	94
C	III	98	88	95	*	105	80

*Analysis not required.

†Percent recovery not applicable since element not detectable in sample.

#Spike omitted.

REFERENCES

1. The Perkin-Elmer Corporation. Analytical Methods for Atomic-Absorption Spectrophotometry. Norwalk, Connecticut, September 1976.

2. McKown, M.M., J.G. Montalvo, and D.V. Brady, BLM Progress Report I, MAFLA Baseline Environmental Survey. BLM Project No. 08550-CT-4-15, Bureau of Land Management, Washington, D.C., December 20, 1974.

3. Davison, R.L., D.F.S. Natusch, J.R. Wallace, and C.A. Evans, Jr. Trace Elements in Fly Ash: Dependence of Concentration on Particle Size. Env. Sci. Tech. 8(13):1107-11113, 1974.

4. Barnes, H.L., and S.B. Romberger, Chemical Aspects of Acid Mine Drainage. J. Water Pollution Control Fed. 40:371-384, 1968.

5. Snell, F.D., editor. Encyclopedia of Industrial Chemical Analysis. Vol. 17, Wiley Inter-Science, Somerset, N.J., 1973. pp. 66-67.

6. Klein, R., Jr., and C. Hack, Standard Additions: Uses and Limitations in Spectrophotometric Analysis. Amer. Lab. 9(7):21-27, 1977.

7. Koirtyohann, S.R., and E.E. Pickett, Spectral Interferences in Atomic Absorption Spectrometry. Anal. Chem. 38:585-587, 1966.

8. Bano, F.J. The Determination of Trace Amounts of Barium in Calcium Carbonate by Atomic-Absorption Spectrophotometry. Analyst 98:655-658, 1973.

9. Cioni, R., A. Mazzucotelli, and G. Ottonello, Interference Effects in the Determination of Barium in Silicates by Flame Atomic-Absorption Spectrophotometry. Analyst 101:956-960, 1976.

10. Fleet, B., V. Liberty, and T.S. West, A Study of Some Matrix Effects in the Determination of Beryllium by Atomic Absorption Spectroscopy in the Nitrous Oxide Acetylene Flame. Talanta 17:203-210, 1970.

11. Sirdiropoulos, N. The Determination of Calcium in Chrome Refractories by Atomic Absorption Spectroscopy. Analyst 94:389, 1969.

12. Rawa, J.A., and E.L. Henn, Interference effects in the determination of Chromium by Atomic Absorption. Amer. Lab. 9(8):31-34, 36, 38, 1977.

13. Chakrabarti, C.L., The Atomic Absorption Spectroscopy of Selenium. Anal. Chim. Acta 42:379-387, 1968.

14. Kirkbright, G.F., and L. Ranson, Use of the Nitrous Oxide-Acetylene Flame for Determination of Arsenic and Selenium by Atomic Absorption Spectrometry. Anal. Chem. 43:1238-1241, 1971.

15. Martin, T.D., and J.F. Kopp, Determining Selenium in Water, Wastewater, Sediment, and Sludge by Flameless Atomic Absorption Spectroscopy. At. Absorp. Newsl. 14:109-116, 1975.

16. Fernandez, F.J., and D.C. Manning, The Determination of Arsenic at Sub-Microgram Levels by Atomic Absorption Spectrophotometry. At. Absorp. Newsl. 10:86-88, 1971.

17. Pierce, F.D., T.C., Lamoreaux, H.R. Brown, and R.S. Fraser, An Automated Technique for the Submicrogram Determination of Selenium and Arsenic in Surface Water by Atomic Absorption Spectroscopy. Appl. Spectroscopy 30:38-42, 1976.

18. Pierce, F.D., and H.R. Brown, Comparison of Inorganic Interferences in Atomic Absorption Spectrometric Determination of Arsenic and Selenium. Anal. Chem. 49:1417-1422, 1977.

19. Yotɛ', J., R. Avni, and M. Stiller, Elimination of Phosphate Interference in Flame Photometric Determination of Strontium and Barium. Anal. Chim. Acta 28:331-335, 1963.

20. Zander, A.T., Factors Influencing Accuracy in Background-Correcter AAS. Amer. Lab. 8(11):11-22, 1976.

21. McKown, M.M., and J.G. Montalvo, The Quality Control of Trace Metal Analysis for the MAFLA Environmental Survey BLM Contract #08550-CT-4-15 Bureau of Land Management, Washington, D.C., August 1, 1975.

PROCEDURE FOR METAL ANALYSIS OF SEDIMENTS

Environmental Protection Agency
Region IV, Surveillance and Analysis Division
Chemical Services Branch

Tentative Digestion of Sediments for Metal Analysis

June 28, 1973

1. Weigh 1 to 2 g of dry (103°C) sediment into a 250 ml Erlenmeyer flask.
2. Add 50 ml water, 0.5 ml conc HNO_3, and 5 ml conc HCl.
3. Heat at 95°C for 15 min.
4. Cool and clarify sample by filtering or centrifuging.
5. Dilute to 100 ml.
6. Proceed with atomic absorption analyses for Pb, Zn, Mn, Cd, Cu, Ni, and Cr.

GSRI ALTERATIONS*

1. 4 g of dry sediment was used.
2. 75 ml of water, 1.0 ml conc. HNO_3, and 10 ml conc. HCl were added.
3. Heating at 95°C was continued until volume was reduced to 10 to 15 ml (approximately 3 hr).
4. Filtration rather than centrifugation was performed.
5. The final dilution volume was 50 ml.

*Changes described were effected in order to improve accuracy and detection limits.